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Research and Development Needs

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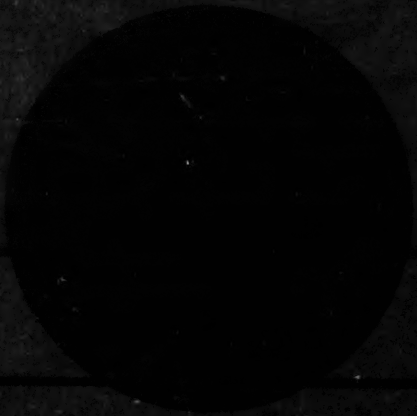

Panel on Fates of Pollutants

Environmental Research Assessment Committee

Commission on Natural Resources

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Analytical Studies
for the U.S.
Environmental Protection Agency

Fates of Pollutants

RESEARCH AND DEVELOPMENT NEEDS

**A Report of the Panel on
Fates of Pollutants
to the Environmental Research
Assessment Committee**

**Commission on Natural Resources
National Research Council**

**NATIONAL ACADEMY OF SCIENCES
Washington, D.C. 1977**

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NOTICE

This report is one of several commissioned by the Environmental Research Assessment Committee for use in its study of the role of research and development in regulatory decision making in EPA. The views expressed herein are those of the Panel on Fates of Pollutants and do not necessarily represent those of the Committee.

The project of which this report is a part was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the Panel responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by the Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

This study was supported by the
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PREFACE

The Panel on Fates of Pollutants was one of four panels commissioned by the Environmental Research Assessment Committee (ERAC) to identify scientific and technical information needed for effective regulatory decision making. The reports of the panels are part of the assessment by ERAC of the role of research and development in EPA, an analytical assessment that is, itself, one part of a more extensive study by the National Research Council of the acquisition and use of scientific and technical information by EPA in its regulatory decision making.

The prime objective of the ERAC study was to examine the processes by which information is acquired by EPA through research and development. Because these processes have both managerial and scientific aspects, the Committee divided its work into two parts. One part, concerned with the organization, coordination, and management of research and development to support the Agency's mission, is the subject of a separate report by ERAC itself. The other, which deals with the identification of technical opportunities for research and with strategies for guiding research planning, was divided among the four panels. The report of the Panel on Sources and Control Techniques deals with research needed on the generation of residuals and strategies for their control. The report of the Panel on Effects of Ambient Environmental Quality deals with research needed on the effects of environmental pollution on living and nonliving things. The report of the Panel on Environmental Impacts of Resources Management deals with research needed on the environmental consequences associated with the development and use of natural resources. (See reference list on page 32 for full titles of these reports.)

This report, prepared by the Panel on Fates of Pollutants, deals with research needed on the transport, transformation, and accumulation of pollutants in the environment. In its charge to the Panel on Fates of

Pollutants, the ERAC asked the Panel to identify fundamental needs for research that will produce scientific and technical information of value to environmental decision making on all the processes that determine the disposition of pollutants in the environment, from their points of introduction to their encounters with receptors. Ultimately, the understanding of these processes will permit the development of predictive models that may be useful for forecasting the consequences of specific discharges, for assessing the levels of risk associated with alternative control strategies, and for establishing emission standards. Each of these objectives is within the scope of EPA's regulatory responsibilities, and it is to attain them that EPA conducts research on the fates of pollutants.

The proliferation of materials, and physical, chemical, and biological phenomena involved in this panel's task made it undesirable to develop listings of research needs for each topic followed by attempts at establishing priorities. Within most specific areas, lists of recommendations for research have already been assembled in a wide variety of specialties; collectively they represent a greater degree of coverage than this panel might have been able to achieve. Rather, the Panel chose to look for recurrent themes emerging from the activities within the field and to recommend ways in which this research might be most effectively pursued.

The Environmental Research Assessment Committee wishes to express its appreciation for the contributions made by the members of the Panel on Fates of Pollutants in the preparation of this report, for the cooperation of the members of the various agencies and institutions, and for the assistance and support of Dr. Stanley Dagley of the University of Minnesota, and Dr. Joseph R. Lakowicz of the Freshwater Biological Institute, who served as consultants. We also wish to acknowledge the contributions made by the staff, particularly the dedicated work of Ms. Karen M. Slimak who, as Staff Officer for this panel, provided invaluable support and editorial assistance.

John M. Neuhold
Chairman
Environmental Research Assessment Committee

ENVIRONMENTAL RESEARCH ASSESSMENT COMMITTEE

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Clifford S. Russell, Director of the Institutions and Public Decisions Division, Resources for the Future, Inc.

Richard J. Sullivan, Richard J. Sullivan Associates, Hamilton Square, New Jersey.

PANEL ON FATES OF POLLUTANTS

A.W. Castleman, Jr.* (Chairman), Professor of Chemistry and Fellow of the Cooperative Institute for Research in Environmental Sciences, University of Colorado.

George M. Hidy* (Vice Chairman), Vice President and General Manager, Environmental Research and Technology, Inc., Westlake Village, California.

Charles F. Eno, Professor and Chairman, Soil Science Department, University of Florida.

E. Paul Lichtenstein, Professor, Department of Entomology, University of Wisconsin, Madison, Wisconsin.

Theodore G. Metcalf, Professor of Microbiology, University of New Hampshire.

James J. Morgan, Professor of Environmental Engineering Science, California Institute of Technology.

Donald J. O'Connor, Professor of Environmental Engineering and Science, Manhattan College.

Robert V. O'Neill, Systems Ecologist, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

John M. Wood, Director, Freshwater Biological Institute, University of Minnesota.

Karen M. Slimak, Staff Officer.

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* Joint member of the Panel and the Environmental Research Assessment Committee.

SUMMARY

This report is concerned with research aimed at describing the behavior of pollutants once they have been released into the environment. The Panel has examined the physical, chemical, and biological processes involved in the dispersion and transformation of pollutants and the mechanisms of their accumulation in the environment. There is a continuing need for this kind of effort to (a) support the selection of pollutants for monitoring, (b) identify key species of significant hazards, (c) measure the levels of exposure of key pollutant species, and (d) estimate the rate of removal of toxic materials from the environment.

The principal objectives of this report are to:

- suggest a systematic method for identification and organization of existing knowledge and of priority research,
- apply the method to selected classes of pollutants for illustration of the suggested planning principles, and
- comment on the limitations and needs in government research administration and management.

Although this report is directed primarily to the Environmental Research Assessment Committee of the National Research Council, it may be useful to the general reader who has interests in this area of research. The report is not intended to be a definitive review of the history and future of fates of pollutants research.

BIOGEOCHEMICAL CYCLES AND RESEARCH PLANNING

A major limitation of the present legislative outlook on pollutants is the failure to recognize the importance of the rates of change or transformation and the transport of materials in the environment. Basically, accounting for these concepts requires that standards be set by exposure, since key pollutants can be chemical end products rather than direct emissions from a source.

Essentially all materials entering the environment move through it over pathways characterized by different time periods until they complete a biogeochemical cycle of change or movement.

The concept of a biogeochemical cycle is recommended as a basic approach in the design of research programs and in predictive modeling of specific pollutants. By extrapolation from the behavior of a well-studied pollutant to a less well-studied but similar material, the areas where research is most important may be determined. The cycle then becomes a planning tool as well as a means of organizing information. This approach is particularly useful because it emphasizes the kinetic aspects of environmental processes. Biogeochemical cycles, which consider the behavior of a substance in the context of its total environmental transport and transformation, should also be useful for structuring monitoring programs, since the most appropriate species and sites for monitoring are more likely to be chosen when the dynamics of the environmental processes are taken into consideration than when a static view is taken.

Based on its consideration of the concept of biogeochemical cycles, the Panel has identified the following general priority needs for research on the fates of pollutants: (a) quantification of the rates of change, i.e., the "dynamics" of concentration and transformation; (b) metabolism of pollutants; and (c) transport of pollutants between air and water, between air and soil, between soil and water, and within the soil matrix.

The Panel studied in detail the biogeochemical cycles of several specific substances falling into one of the following classes of pollutants: naturally-occurring essential materials, naturally-occurring nonessential materials, synthetic chemicals, and biological pollutants. (Naturally-occurring essential materials are required for sustaining life, while nonessential materials are not.) Specific research needs identified in these studies are summarized in Chapter 3, which outlines the principles of the cycle approach. Some details of the studies of the four major classes of materials are contained in the Appendixes.

MANAGEMENT AND COORDINATION OF RESEARCH

The Panel did not have the manpower and time to make an exhaustive study of the management of research on the fates of pollutants. However, the members' past experience provided insight into some current limitations in the management of the national program. The Panel believes that the existing mechanisms for coordinating government research from planning to completion must be improved. In the course of this study, the Panel observed that, in general, there appear to be ample financial and institutional resources available for research on the fates of pollutants relative to equally important needs for other environmental studies. However, the distribution of resources among areas of specialty seems to be unbalanced to meet the requirements of certain high-priority needs that now demand attention. For instance, there appears to be a heavy emphasis on the physical transport in fluids (air and water) and on the chemistry of atmospheric pollutants as compared with the processes of biological transformation. Where knowledge is extensive, management attention is required to focus on research to fill critical gaps in information.

The Panel wishes to stress the following points, which are elaborated upon in the report.

- A detailed inventory should be made of research programs inside and outside of government on the fates of pollutants. This survey should include a critical review of ongoing activities, and identify duplications of effort and neglected areas.

- The research inventory should be used with the biogeochemical cycle framework as a basis for creating an interagency, national research plan that takes into account the requirements of both long-term and short-term research objectives.

- The applicability of research on the fates of pollutants to environmental decision making should be recognized and emphasized when priorities are established for research planning and implementation.

- Research on the fates of pollutants requires an integrated, complementary program of laboratory and field studies. The laboratory offers control of relevant variables, while the field gives the perspective of the complexities of the real environment.

- Recognition must be given to the needs for geographically specific research programs aimed at resolution of major problems unique to respective parts of the nation.

- To obtain timely, accurate technological information for use in environmental decision making, peer review of research plans and results is essential. We recommend the enhancement of such peer advisory activity. The process should include progressive internal review as well as testing for acceptance in the public scientific literature.

- The implementation of research must be accompanied by adequate manpower training in special, emerging areas of environmental technology.

- Recognition must be given to the distinction between classes of generic research requiring a long time to complete, and short term programs that are highly oriented toward supporting a pending regulatory decision.

- Budgeting must be flexible to provide for long-term research requirements, as well as for short-term, high-priority projects to explore new problems of great potential impact.

CHAPTER 1

INTRODUCTION

This document is the final report of a panel of the Environmental Research Assessment Committee concerned with research on the fates of pollutants in the environment, including all processes determining the disposition of pollutants from their point of entry into the environment, to and including their encounter with the receptor, represented by man and the biosphere. The complex pattern of movement of a substance through the environment, its physical transport and its physical, chemical, and biological transformation and accumulation, is called its biogeochemical cycle. Some such cycles are, indeed, closed, although usually only through a complex web and over a long period of time; the carbon cycle is an example. Others, such as those of degradable synthetic chemicals, are not. By using the term biogeochemical cycle we mean a complete accounting of all the interrelated processes that affect a given substance in the environment, including a description of the rates at which these processes occur. It is, simply, a system for mass accounting as substances move throughout the biosphere and geosphere. In this context, the Panel considered those research areas dealing with the physical, chemical, and biological processes that influence the nature of the transformations governing the chemical and physical states of the pollutants leading to the hazards they pose to man and his environment. Consideration was given to detailing the research needed to establish the rates of transport and disposal in the environment, bioaccumulation, degradation, and mutual interactions of important pollutants. However, it was soon recognized that creating such a list would not be a task that the Panel could complete with the resources available to it. Furthermore, it was the belief of both the Panel and of federal personnel with whom the Panel consulted, that the development of a "monthly crisis list" of environmental research topics warranting attention would be of relatively little value and soon outdated.

Instead, we recognized an increasing need to organize environmental research systematically along both short-term and long-term priorities. There always will be a need to investigate individual pollutants as new emission products are identified. However, a considerable increase in the efficiency of assessing the impacts of new materials should be achievable by systematic classification of environmental processes using our present knowledge of physics and chemistry.

An additional important requirement for research management is information on the operating structures of the sponsoring agencies that implement programs investigating the fates of pollutants. The members of the Panel considered features that lay within their experience: government planning and management, the manpower and institutional needs to conduct such research, and the needs for quality assurance and peer review.

In assessing general research needs on the fates of pollutants, it was necessary to consider such diverse aspects as the nature of environmental media; the movement of various compounds through the air, water, soil, and food chain; the transport, uptake, and fate of viruses; and the dispersion of noise and various forms of electromagnetic radiation in the environment. We have found it useful to consider two broad classifications for pollutants: namely, materials and energy.

In this report, the materials category comprises chemicals, both naturally occurring and synthetic, and biological materials, including bacteria and viruses. We are all aware that the continual input of any substance into the environment will create a potentially adverse effect if the resulting concentration far exceeds that which results from natural processes. Ultimately, the effects can manifest themselves as direct hazards to human health, as changes in the quantity or quality of components of the food chain, or as climatic changes with concomitant, universal impacts.

Likewise, the introduction of various forms of energy into the environment can constitute pollution. Noise at high levels can influence the productivity of workers and under severe circumstances impair hearing. Electromagnetic radiation in the form of light can affect vision and alter the metabolism of sensitive receptors. At higher energies, electromagnetic radiation can cause direct biological damage and even mutagenesis. Energy in the form of heat leads to local temperature changes that may directly influence rates of chemical reactions, food supplies, and the life cycles of organisms.

In what follows, many of the material pollutants are discussed in terms of transport and rate or kinetic processes. There is often a complex environmental cycle for a given species and its disposition is not easily detailed and assessed. Energy, on the other hand, while influencing natural processes that, in turn, influence the cycling of materials, dissipates readily and its "migration" is rather straightforward and predictable. The Panel deemed an in-depth consideration of forms of energy as pollutants unwarranted, since, by comparison to materials pollutants, the mechanisms and rates of dispersal are largely known. The needs for future research on energy as pollution lie primarily in the areas of sources and effects, both topics that lie outside the scope of the Panel on Fates of Pollutants (see NRC 1977a, 1977d).

Much of the emphasis of federal environmental research programs has been focused on the measurement of levels of pollutants directly discharged into the environment, on control of such emissions, and on determining the effects of pollutants upon receptors. While this direction provides important data, undue emphasis has been given to these areas at the expense of research devoted to the fates of pollutants. The result is a general gap in knowledge in an area that is vital to predicting the changes in exposure levels resulting from a change in the quantity or quality of pollutants discharged. Only by establishing a better understanding of the chemical, physical, and biological processes governing the fates of pollutants can the link between sources and receptors be quantified. The optimal design of pollution control strategy and environmental monitoring programs hinges on having such information and understanding.

The movement of a material through the environment is influenced by several factors, including the rates of inputs and transport and kinetic processes. Kinetic processes include chemical, physical, and biological transformations, accumulations, and removal. The rate-controlling step often determines whether a material, or the environmental cycle that influences its distribution, is of major importance.

At present, characterization of the mechanisms of both chemical and physical conversions and biological transformations are at rudimentary stages of development. Rectification of this situation warrants prime attention. Data on the rates and mechanisms of conversions and on rates of transport are urgently needed as inputs to quantitative models developed to assess the ultimate fate and hazard posed by environmental pollutants. Without such data it is impossible to assess adequately the levels and durations of exposure; consequently the development of fair and meaningful environmental regulation is inhibited.

To address the desired aspects of the fates of pollutants some aspects of research management are considered in Chapter 2. Chapter 3 discusses in depth the biogeochemical cycle as a tool for organizing information and planning. The Appendixes illustrate ways in which our recommended methods of identifying and organizing priority research can be applied to some important classes of pollutants.

CHAPTER 2

GENERAL IMPRESSIONS OF MANAGEMENT PRACTICES

This study has resulted in some impressions about the milieu in which research on fates of pollutants is supported and conducted by the federal government. Important problems related to the coordination of research, the resources devoted to it, and the setting of priorities must be addressed if useful and accurate information on the fates of pollutants is to be obtained quickly enough to be useful in future decisions. This chapter addresses the most significant of these problems identified by the Panel.

INVENTORY OF RESEARCH PROJECTS

The Panel spent considerable time discussing aspects of the management of research on the fates of pollutants. We experienced great difficulty in obtaining an inventory of current research. A catalog covering the work sponsored by many agencies, including accurate project descriptions, funding levels, and specific objectives, does not exist. As a consequence, it was very difficult to provide specific comments and suggestions about resource levels and improvement or redistribution of programs to meet needs in this area of research.

Environmental research, despite its popular identification with the Environmental Protection Agency (EPA), is sponsored and managed by more than a dozen federal agencies, several of which have been undertaking such studies for many years prior to EPA's organization. Many of these agencies are conducting or funding research on the fates of pollutants; examples include the Energy Research and Development Administration (formerly the Atomic Energy Commission), the Department of Defense, the National Institutes of Health, the National Science Foundation, and the Department of Agriculture. As a result of the multi-agency sponsorship of fates research, a wide variety of programs exists. Many of these programs are not well-documented, or even known to workers in similar areas of scientific discipline. The management of the government's programs is greatly inhibited by the lack of an overview of fates research completed or in progress.

As a first step toward better management of this research, there should be created a thorough, systematic inventory of the intramural and extramural research being funded privately and by the government. The purpose of such an inventory would be to identify the nature of all agencies involved in fates research, the total amount of money being spent, the extent of private funding, and the distribution of emphasis within the field; this last will indicate the degree of coverage, areas of duplication, and areas where gaps exist. The inventory will provide evidence of the areas most in need of a cooperative federal research effort.

In a next step, methods of coordination and cooperation among federal, state, local, and private research agencies should be instituted to reduce needless duplication, eliminate gaps in coverage, and assure that the depth of coverage in each area is adequate. Implementation should involve a special full-time staff, whose appointment is defined by agency management to coordinate and integrate fates research programs. The program management staff should be reinforced by active interagency committees and peer group advisors. As coordination improves, money, institutional resources, and time should be used more efficiently. Cooperation among agencies in planning research programs and in exchanging information is important if research on fates of pollutants is to progress at a productive rate to meet the needs of decision making for environmental protection.

One advantage of improved coordination in fates research would be the opportunity for improved homogeneity in conduct of large research projects and for diversity where needed. The Panel believes that this research would be greatly enhanced by coordinating the methods used in similar studies, the formats for collection, handling, and presentation of data, and the criteria used in selecting sites for field studies. This coordination should be encouraged wherever possible without suppressing the ingenuity and vitality of alternative approaches to problem solving.

PRIORITIES IN RESEARCH

Even though research on fates of pollutants is often classified as fundamental research, it is directly relevant to environmental management, since it influences decisions on the development of control technologies, the application of monitoring and control strategies, and the marketing of chemicals, and describes the extent to which receptors are likely to be exposed to pollutants. Information on the behavior of substances in the environment provides the vital link between the source of a substance and the concentrations to which the population is exposed. Research on fates of pollutants, then, is directly relevant to environmental decision making and is in fact of strategic importance to it.

Regardless of the source of funding, whether public agencies or private industry, it is important that the significance of specific research projects be recognized and identified in achieving organizational objectives. Without such recognition, this area of research cannot be given its due priority for both short- and long-term planning. In the past, research on fates of pollutants has often been considered to be basic scientific work, as contrasted with applied research, and mission-oriented agencies have tended not to support it. This is especially the case for biochemical transformation processes and multimedia interactions influencing biological processes. When its strategic importance is recognized, fates research is seen to be compatible with regulatory missions and its support can be planned intelligently.

The large number of participating agencies have different objectives and conflicting philosophies regarding programs in fates research. Yet many of the problem areas being investigated are of mutual interest to many of the agencies, sometimes in conflicting ways. As a consequence, there appears to be fragmentation and dispersal of resources on the one hand, with duplication of effort on the other. Duplication of research effort is a healthy and desirable feature of programming when fundamental issues of behavior are of concern. However, duplication of larger programs to measure characteristics or changes is not warranted where basic processes and measurement methods are largely agreed upon. In the past few years, there has been overlap and duplication in government programs aimed at improving knowledge of the behavior of regulated pollutants by monitoring and surveillance. As a result of legislative action over the past decade, heavy emphasis has been placed on enhancement of detailed knowledge of physical transport involving fluid motion. Considerable effort also has focused on the chemical changes of pollutants in the atmosphere. Much less activity has been planned and organized to study interactions between the soil-air and soil-water mixed media, or biochemical transformations that may influence food chains and supplies of potable water, and consequently the sustenance of human life. At the present time, the vehicles for identifying overall priorities and the strengths or weaknesses in our knowledge of the fates of pollutants are informal and generally do not work efficiently.

Government agencies have recognized the need for coordination of research to avoid unnecessary duplication and account for gaps in programs. To provide for such coordination, ad hoc interagency committees and extramural peer advisory committees have been formed. These entities have largely failed to provide the needed guidance for fates research. There is a need to improve these advisory functions, and to ensure that the policy makers act on such advice.

DYNAMICS OF POLLUTANTS AND BIOGEOCHEMICAL CYCLES

A static view of the environment is the major reason that many sampling and analysis programs have not provided useful information on the distribution of pollutants in the environment. Biogeochemical processes are dynamic; their influences on the transport and transformation of pollutants cause continuing changes in concentrations and molecular structure. In fact, transport and transformation can both be described in terms of rates of change (kinetics).

The Panel recommends that the dynamic view of the environment be a major contributor to the development of management criteria for sampling programs and that these programs be designed to further our understanding about the rates of transport and transformation of pollutants as well as to identify their presence. The Panel also feels that with a better selection of key environmental components for measurement, less monitoring effort may be required. The capabilities thus freed should be channeled into studies of kinetic processes.

Too much emphasis has been placed on investigating the details of relatively well-known processes, while gaps still exist in our understanding of many basic biogeochemical cycles. EPA's present programs are heavily weighted toward air chemistry and the dynamics of fluid transport. Since these areas are relatively well understood at present, research should be highly selective and focused to fill important information gaps. For example, the key to an improved theory for gas phase air chemistry is now well known to be the behavior of hydroxyl radicals. Research is needed to measure concentrations of these radicals to verify the conclusions of new kinetic models. Another example is the need for improved information about air motion over distances of hundreds of kilometers to improve airshed pollution analysis.

Continued studies of presently regulated pollutants and well-known but unregulated pollutants have been overstressed. Funds for research in the fates area seem to be crisis-oriented. When a certain pollutant receives national attention, grants and contracts for study of that pollutant receive greatly increased funding over a short term. However, funds for problem areas identified systematically in the development of long-term research objectives may be sacrificed. While crisis-related studies are useful for essential decisions on a specific substance, they may yield little of value for intelligent impact assessment when a new series of pollutants evokes interest. Although short-term surges of research on individual substances in response to crises will continue, these should be minimized as much as possible so that progress may be made toward research on broad classes of pollutant compounds in anticipation of future environmental problems. There is a definite need to structure programs so that, while specific information is obtained, our broad understanding of the behavior of pollutants in the environment will improve.

The Panel recommends the use of biogeochemical cycles as a means for organizing research programs, for determining important gaps in information, for comparing pollutants, for summarizing available information, for establishing the best approach for conducting research, and for assessing priorities in research. Greater use should be made of our knowledge of natural cycles and the total environmental transport of well-studied pollutants in planning for future research needs. The concept of the biogeochemical cycle offers a useful framework for identification of fates research problems. Major pollutant emissions should be identified and, with the help of existing knowledge, traced through the environment by the cycle approach. Areas of major uncertainty in lifetimes, intermediate species, or end products of emissions should then be identified.

The cycle approach is discussed in greater detail in Chapter 3 of this report. It is based on the following assumptions:

1. Biological, chemical, and physical processes act continually to transport, synthesize, and degrade substances. These processes also affect pollutants released to the environment. The fate of the pollutants (transport and transformation in the environment) is determined by the response of that pollutant to the biogeochemical processes.

2. Although each pollutant behaves uniquely in the environment, similarities exist; the greater the physical and chemical similarity of two compounds, the more similar their transport and transformation in the environment will be. When the environmental fate and the chemical and physical properties of a well-known chemical pollutant are summarized, these data may be applied to a similar, less well-studied pollutant and the most important needs for research identified for the new material. Therefore, the cycle approach may be used to formulate hypotheses (to be tested

through research) about the behavior of new substances in the environment.

The cycle model is particularly useful because each substance is viewed in the context of the changes that it undergoes in the environment; i.e., kinetic processes are emphasized. Gaps in knowledge are also easily identified in principle.

The Panel has used the concept of biogeochemical cycles in its assessment of needs for research on fates of pollutants. Several important areas were immediately apparent. The area in greatest need of increased research support is kinetics--the rates of transport and transformation of pollutants. In many cases the basic pathways have been determined, and important sites of accumulation identified, but associated rates have not been determined. This information is vital to the evaluation of a pollution problem and to the selection of appropriate regulatory approaches.

Increased studies of intermedia processes and of the interactions among pollutants are needed. There is often a coupling between the environmental cycles of several substances, and a change in the concentration of one compound may drastically affect the behavior of others (see, for example, Appendix B). In studies of the interactions among pollutants, it is especially important to consider a given pollutant in terms of biogeochemical cycles.

Finally, more studies are needed of the transformation and transport of pollutants as influenced by geographical differences. Variations across the United States in emission patterns, climatic influences, and soil and water characteristics significantly affect the chemistry of the air, soil, and water and intermedia processes.

OTHER CONSIDERATIONS

The Panel makes four further recommendations for the development and implementation of research on fates of pollutants. First, in addition to a balance among long- and short-term studies, and among regional and site-specific studies, a balanced program of research on the fates of pollutants requires a combination of both field and laboratory investigations. Neither of these methods can, by itself, provide conclusive information about the complex interactions that occur in the environment. The laboratory permits control and simplification, while the field offers the full complexities of the environment. Both are needed to unravel the mysteries of nature; they are complementary techniques that, when combined, hold promise for solving practical problems scientifically.

Second, in current and future investigations, multidisciplinary efforts must be increased because of the many scientific complexities involved. We need an integrated approach to research that considers the many facets of the environment as opposed to a narrow, fragmented study of singular aspects of pollutant behavior. The use of interdisciplinary teams with management experience in many of the environmental programs should substantially enhance the chances of obtaining the necessary knowledge to quantify dynamic processes in the environment.

Third, increased use of peer review is recommended to aid in improving the quality and credibility of completed research. Such activities should include internal scrutiny of programs by advisors, and the publication of research in the open scientific literature. Internal peer review has been used effectively by the National Institutes of Health among other agencies; broad application of such procedures to environmental research is recommended. In-house publications of federal agencies generally are not reviewed externally, and are not acceptable to the scientific community as a whole. The pressure for continual upgrading of research resulting from such open review is important to maintenance of continued quality of programs and is strongly recommended.

Fourth, programs must be continued and enhanced to train skilled investigators in key areas of environmental science and technology. In the past few years many training grants have been terminated. With the continued emergence of interdisciplinary studies in new areas of environmental science, there is a great need to prepare workers to respond to new problem areas. The lack of trained scientists is especially acute in the biochemical aspects of environmental research. The Congress should re-examine the recent trend to reduce funding for training of scientists, an investment that is essential to maintaining a skilled cadre of workers to attack future environmental problems.

CHAPTER 3

THE CYCLE APPROACH FOR RESEARCH PLANNING AND MANAGEMENT

This chapter elaborates upon the general concept of biogeochemical cycling as a framework in which to plan and manage programs for research on fates of pollutants. First, the important kinetic and transport processes involved in the cycle are defined. Then, material pollutants are divided into four categories--naturally-occurring (biologically) essential materials; naturally-occurring nonessential materials; synthetic materials, and biological pollutants--and described by the features of the biogeochemical cycle typical to each category. Appendixes A, B, C, and D illustrate both the applicability of the cycle approach to these categories of pollutants and its usefulness for applying information on one pollutant or class of pollutants to another. Research needs for these specific examples are also identified.

KINETICS AND TRANSPORT

The migration of a material through the environment and the transformations the material undergoes are influenced by three important factors: inputs, kinetics, and transport. Inputs--the quantity and form of a material and the place where it is discharged into the environment--greatly influence rates and routes of transport and transformation and the levels to which receptors are exposed. Needs for research and development on inputs of materials are considered in detail by the Panel on Sources and Control Techniques (see NRC 1977d), and therefore are not discussed further in this report. Kinetic and transport processes are discussed here in the context of biogeochemical cycles and their relevance to fates research.

Kinetic Processes

Kinetic processes, which occur throughout the environmental system (Figure 3.1), can be described as occurring at specific points in space or as averaged over considerable regions, even the total surface of the earth. Examples are physical, chemical, and biological transformations and diffusion. The rates at which kinetic processes take place are important aspects of biogeochemical cycles.

Particularly important kinetic processes are those that determine the storage of substances in reservoirs and their subsequent remobilization. Accumulations of harmful substances in reservoirs can be a most important determinant of the level and length of time of exposure to which receptors are subjected. Storage or accumulation is possible in the atmosphere, geosphere, hydrosphere, and the biosphere. Some elements, such as nitrogen, are stored in large quantities in the atmosphere, while others are maintained in rock structures of the geosphere. Significant quantities of material may remain dissolved in the oceans or accumulate in sediments. Materials may be accumulated, transformed, and redistributed through biological activity.

The kinetic processes important to a biogeochemical cycle, including the accumulation of pollutants in reservoirs, are dynamic processes, occurring at rates determined by physical and chemical factors. A static view of the environmental system does not consider the rates at which processes occur and can lead to unreliable conclusions about what to monitor. Because of the differences in the kinetics of the system, the concentration of a pollutant undergoing chemical change can remain constant despite the amount of precursor in the environment. Unfortunately, the most accessible and most easily monitored pools may be the least characteristic of the dynamics of a biogeochemical cycle of a hazardous material. For example, the concentration of nutrients in a water column may remain relatively constant while, in fact, large quantities of nutrients are being transferred from sediments to algal biomass.

Consideration of only a single process in a relevant biogeochemical cycle can also lead to faulty conclusions. Looking at just one process in a rather complicated system has, for example, led us to consider burying wastes as a permanent end to their environmental transport. The extensive evidence of the remobilization of buried wastes and their reintroduction into the environment through groundwater is a convincing example of both the dynamic character of the environment and the need for thorough examination

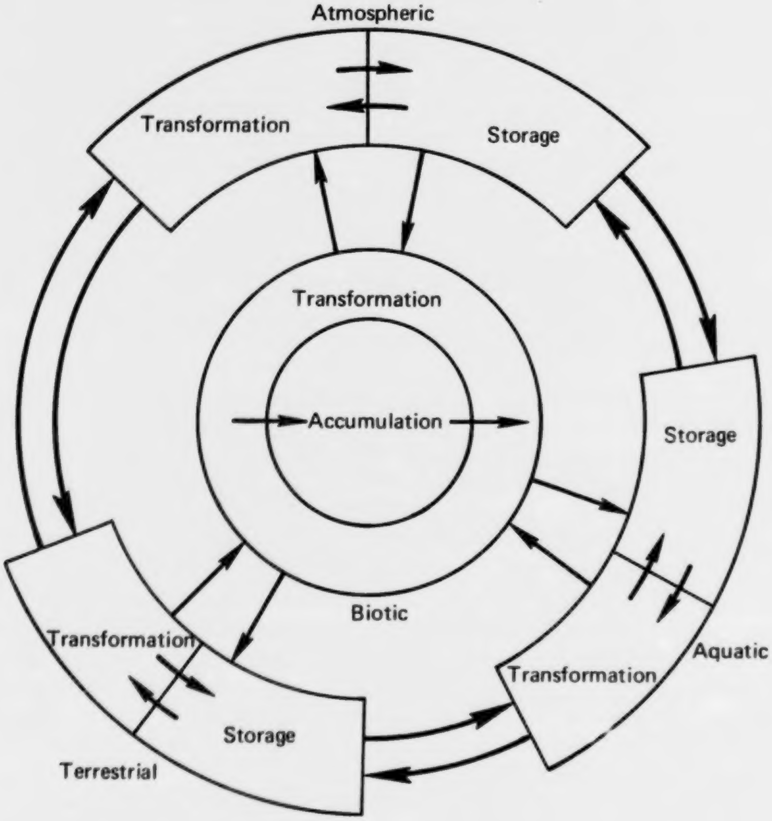

Atmospheric
Transformation
Storage
Transformation
Accumulation
Storage
Biotic
Transformation
Aquatic
Transformation
Storage
Terrestrial

FIGURE 3.1 Physical, Chemical, and Biological Transformations in the Environment

of all relevant environmental processes in an integrating framework.

Kinetic processes that affect the intermedia transfer of substances may be the most poorly understood area of biogeochemical cycles. For example, the lack of basic research on interactions that occur at the interface between the atmosphere and bodies of water is a weak link in our understanding of the effects of atmospheric pollution on water quality. Lack of information on water column/sediment dynamics leads to problems in predicting the rates of transport of some substances between these media. The interaction between the atmosphere and vegetative surfaces, essential to understanding deposition of airborne pollutants, is also a little-known area. The needs for research related to intermedia processes are likely to be more clearly defined if these processes are viewed in the context of a total biogeochemical cycle.

Too often, investigations aimed at elucidation of environmental processes stop after laboratory verification. As mentioned in the previous chapter, field testing of laboratory results is always needed so that specific processes can be considered in the context of the total environmental processes of which they are a part. This is particularly true of kinetic processes, since the rates at which they proceed are determined by environmental parameters. For example, although biomethylation of tin has been observed under laboratory conditions, it has not been found under field conditions. On a larger scale, existing waste treatment facilities are ready-made tools for field testing; they should be used to test the importance of specific processes in the context of the total set of environmental processes occurring around them. Researchers should be more actively and closely involved with these facilities, particularly in evaluating existing facilities and testing new ones.

Accelerated research on environmental kinetic processes could improve predictive capabilities, particularly if it leads to an understanding of how the behavior of one substance can provide a basis for predicting the behavior of new, similar substances. Some predictions can now be made by comparing the fundamental processes of the biogeochemical cycles of similar chemical species.

Physical Transport Processes

The preceding discussion has largely emphasized the kinetic processes associated with the transport and transformation of pollutants at a point in space. Frequently, however, the most important factor is the local concentration of a pollutant as affected by physical processes that move material spatially through the environment.

Atmospheric processes transport material away from point sources of release such as smoke stacks. We have gained some confidence in predicting the movement of airborne pollutants for short distances along dominant wind directions. However, effects of topography on dispersion are still poorly understood and it is not yet possible to predict transport for distances beyond tens of kilometers from a source. Although diffusion and transport processes in the upper atmosphere are known to be important, not enough basic research has been done on upper atmospheric processes to permit estimation of pollutant movement with confidence levels even of ±50 percent.

For many substances, transport of materials suspended or dissolved in water is a key process in their biogeochemical cycling. Runoff or groundwater movement can carry such substances from the point of deposition through streams and rivers to freshwater lakes and ultimately into the oceans. Transport in the oceans is influenced continually by ocean currents of varying magnitude and by important phenomena such as the upwellings along coastal regions.

Even materials of low solubility or substances that are tightly bound to soil particles can continue to be transported as a result of mass movement of soils through erosion. The significant scouring of sediments in streams and small rivers caused by intense storms is thought to be a primary mechanism for transporting such materials as nutrients from watershed systems, even though these events may be relatively infrequent.

Physical transport through the biological system is generally a minor factor in biogeochemical cycling, but can become significant in special cases. The migratory movements of large mammals, for instance, can result in transport of significant quantities of materials. Little is known about this type of transport at present.

ANALYZING THE BEHAVIOR OF POLLUTANTS USING BIOGEOCHEMICAL CYCLES

In this section we define four categories of pollutants and describe how the behavior of substances in these categories might be analyzed in terms of their biogeochemical cycles. Appendixes A, B, C, and D contain more detailed examples of representative cases from each category. The recommendations for research developed from the analyses in the Appendixes are also summarized in this section.

Industrial, organic, physical, and inorganic chemists have been extremely imaginative in the variety of compounds that they have synthesized for the commercial market. It has been difficult, if not impossible, to match their ingenuity with corresponding predictions of the environmental behavior and effects of each new substance or its by-products. Since it is virtually impossible to treat each new pollutant as a special case, some method must be developed to integrate information and to use existing knowledge to extrapolate to significant pollutants as yet unidentified.

The present emphasis of environmental research appears to be on monitoring, controlling emissions, and studying effects on selected receptors of materials falling under regulatory legislation. Monitoring programs spend large amounts of money collecting data that may be of limited use, either because the wrong substances in the wrong forms are observed without quality control of the measurements, or because the information tells little about the behavior of pollutants, much less of the broad classes of interrelated pollutants, in the environment. Available data, moreover, are often not used effectively. At present, knowledge about one substance is not used efficiently to identify productive areas of research for other substances; information about transport and transformation must be translated into a form that makes extrapolation possible. Controlling emissions at the site of discharge and monitoring concentrations of pollutants in the ambient environment leaves a large gap in our understanding of environmental responses to pollutants. It is vital to fill this gap if the link between sources and exposures is to be established, the best control strategy identified, and effective programs for measuring pollutant impact designed.

While a newly-identified pollutant may have unique properties, it is also likely to have some properties of origin, chemistry, or physics in common with other substances about which some things are known. We are not fully exploiting our understanding of such common properties. The biogeochemical cycle offers a convenient, scientific framework for organizing our knowledge so that it can be exploited through extrapolation by hypothesis and testing. In particular, extrapolation of information from a well-studied pollutant to a less well-studied, but similar, material can determine by analogy the areas where research is most likely to be needed. The biogeochemical cycle then can be used as a planning tool as well as a system for organizing information about the behavior of a particular substance.

Fundamental studies of biogeochemical cycles themselves should emphasize common pathways and trends, while applied studies should focus on the behavior of individual pollutants as they come to the foreground. In the context of decision making for environmental protection, the biogeochemical cycles of greatest interest are likely to be site-specific or, at most, regional since local conditions determine the processes and rates that determine the fates of pollutants.

The cycles that describe how pollutants are transported and transformed in the environment are likely to vary depending on whether biological organisms or chemical substances are involved and whether the substances are synthetic or occur naturally and are essential or nonessential to biophysical processes.

Naturally-Occurring Essential Materials

Whether a material is essential or nonessential to metabolic processes is determined primarily by the extent to which organisms require it in order to live and reproduce. Elements or compounds that are essential to nature, that participate in important metabolic processes, become pollutants when they are released into the environment in quantities that put populations or ecosystems under stress. For instance, nutrients in excessive concentrations may stimulate excessive (eutrophic) metabolic activity in natural waters, leading to oxygen depletion and deterioration of water quality. Heavy loadings of phosphorus or nitrogen may stimulate fertilization of natural waters, leading to distortion in the vertical distribution of oxygen, sulfur, and trace metals in deep lakes. In water, high concentrations of such essential trace metals as copper can exert toxic effects on plant and animal populations. Similar considerations apply to nitrogen dioxide, carbon, carbon dioxide, and sulfur dioxide, which occur naturally in the atmosphere, when man-made emissions elevate their concentrations on a regional (carbon, nitrogen dioxide, sulfur dioxide) or a global (carbon dioxide) scale. Although the local impact of this type of pollution may be severe, the potential for complete recovery exists, but severe problems may result if such materials are continuously released at rates in excess of assimilative capacity. In Appendix A the biogeochemical cycles of nitrogen, a naturally-occurring essential chemical, are used to illustrate (a) natural cycling processes, and (b) the ways in which sudden, large increases of essential materials stress environmental systems in discernible ways.

Specific Recommendations for Nitrogen

As a result of its considerations of nitrogen cycles, the Panel makes the following observations and recommendations:

- One of the most important needs for research on nitrogen and its compounds involves the mechanisms and rates of transport among air, water, and soil.

- In the atmosphere, recommended areas for study include (a) intermediate products of NO_x conversion to nitrates, (b) kinetics of NO_x reactions, (c) the importance of ammonia to the formation of particulate nitrates, (d) the amount of organic nitrogen present compared with inorganic nitrogen, and (e) the way in which nitrogen and sulfur processes are coupled in terms of photochemical phenomena and aerosol formation.

- In the soil, recommended areas for study include (a) the role of nitrogen in eutrophication, (b) the relationship of soil properties to nitrate transport and transformation, (c) the influence of seasonal, annual and geographic variations to nitrate movements in soil, and (d) coordinated field and laboratory studies.

- In water, recommended areas for study include (a) the degree and manner in which nutrients become available to the growth of phytoplankton, (b) the exchange between the bed and the water column, (c) the delineation of nitrate transformations by groups of algae, and (d) the transforming mechanisms involved in the occurrence of eutrophication.

Naturally-Occurring Nonessential Materials

Examples of naturally-occurring materials that are not essential to normal life processes are mercury, cadmium, arsenates, and fluorides. Because plants and animals have been exposed to low concentrations of such materials for a long time, they have developed protective mechanisms. Various possibilities for biochemical detoxification include random binding to secondary sites of globular and structural proteins, addition to carrier proteins to facilitate elimination, partial or complete degradation, and formation of coordination complexes. These modifications, in general, facilitate the elimination of the substance or render it less toxic.

Naturally-occurring but nonessential materials have had limited circulation in the environment throughout most of history; they are bound in rock formations, held in subsurface deposits, and so forth. Mining disrupts these associations, and transport during refining, manufacture, and consumer use alters chemical forms and exposes these materials to the environment at levels that stress assimilative capacity.

The environmental migrations of substances in the category of naturally-occurring nonessential chemicals are discussed in detail in Appendix B, where heavy metals are used as an example. Chemicals in this category are good examples of the results of man-made additions to preexisting cycles. They differ from nitrates (the example used in Appendix A for naturally-occurring essential materials) in that they are not ubiquitous. Their metabolism is limited to detoxification and elimination processes; by definition they do not become an integral part of essential life processes. They tend to bioaccumulate through food webs. These materials are useful in illustrating the importance of the dynamics of environmental processes, and are good examples of the importance of the dispersal of materials that takes place while they are adsorbed on particular surfaces.

Specific Recommendations for Heavy Metals

As a result of its considerations of the cycles of heavy metals, the Panel makes the following observations and recommendations:

- Residence times--and hence exposures--depend on mobilization of metal ions or their derivatives from particulate matter in water and sediments. The kinetic aspects of chemically and biologically mediated transport need to be studied for metals of potential environmental importance (e.g., cadmium).

- Transport by sedimentation and particle resuspension depends on flocculation of particles in natural waters. This process is too poorly understood to enable prediction. Work with mixtures of natural particles and pollutant particles should be undertaken.

- Chemical speciation of heavy metal compounds is crucial to understanding their transport and transformation in the environment. The following studies are critical: (a) ion association, (b) dissociation in freshwater and seawater, (c) oxidation-reduction reactions, and (d) distribution of chemicals between solution and solid particles by adsorption-desorption, precipitation-dissolution, and ion-exchange processes.

- The chemical and biological evolution of toxic metalalkyl compounds is poorly documented. These are environmentally important and require investigation. The work can be illustrated by methylmercury as well as by other biomethylated elements that are not well understood. Field studies should be extended on the movement of metalalkyls in the food chain, with identification of active facilitated transport and diffusion controlled processes. Kinetic studies on membrane transport and partition of metalalkyls in biological systems are also needed for elucidating the bioaccumulation of this group of compounds.

- Three additional areas require study in order to predict the movement of heavy metals in the biosphere. These needs, which stress the importance of the partitioning of heavy metals among mineral and organic fractions of soil and sediment, are: (1) behavior in sediment, suspended solids, and soil sinks, (2) biological availability for these sinks, and (3) direct availability to biota from water and air.

Synthetic Materials

Synthetic materials (discussed in Appendix C) result from the recombination of natural materials into substances that are foreign to natural systems. Plutonium and carbon tetrachloride are examples. No synthetic material is essential to the normal functioning of biophysical processes; therefore, there is no level of exposure that can be considered beneficial. When these materials are not completely inert, they are biophysically disruptive to some degree at all levels of exposure. Because synthetic materials are completely foreign to biological systems, biochemical responses are limited. Cellular penetration generally occurs by passive diffusion through the membrane, a process that is independent of biotic control. In most cases, once inside the cell the synthetic materials are primarily accumulated unchanged. This is especially true of lipid-soluble organic and organometallic compounds. To the extent that a compound is chemically and structurally similar to a natural material, active transport processes and biological modification may occur.

The cycles of synthetic materials are important because they illustrate the ways in which natural processes act on substances that are not part of natural cycles. Once released to the environment, a synthetic chemical is subjected to biogeochemical processes that eventually convert it to naturally-occurring by-products that enter their own cycles. Therefore, the term "cycle," when applied to a synthetic compound, actually refers to the routes and rates of transport or transformation between discharge and incorporation into cycles of naturally-occurring substances. Unless there is continual production of synthetic compounds, cycling of the parent material stops at some point. Synthetic materials may be quickly incorporated into natural cycles if they are similar to naturally-occurring substances. Some synthetics, of course, may be quite persistent.

Appendix C discusses synthetic organic chemicals and their biogeochemical cycles.

Specific Recommendations for Organic Chemicals

As a result of its considerations of the cycles of organic chemicals, the Panel makes the following observations and recommendations:

- Synthetic compounds must be evaluated and tested for persistence and for their potential for bioaccumulation.

- More fundamental research is needed on the kinetics of the processes of diffusion and partition of individual compounds. Once this fundamental information is obtained for a group of compounds with different chemical structure, then it should be possible to predict rates of bioaccumulation for individual compounds as they are manufactured and released.

- Further studies are needed to determine the relationships between physical and chemical properties of synthetic organic compounds and the way these properties influence the behavior of the materials in the environment.

- Delineation of photochemical reactions with synthetic compounds should be carried out to determine whether photochemical products are more or less toxic than the parent synthetic compound.

- Pesticides and insecticides should be designed that more closely represent the natural products that microorganisms can degrade in the biosphere. Special emphasis should be placed on oxidative degradation, since anaerobic bacteria are not as widespread as aerobic bacteria.

- A biochemical approach to biodegradability should be adopted, together with the selection of mutants that show increased degradative versatility toward synthetic compounds.

- A study of the degradation of natural products that contain halogen substituents is needed to obtain more knowledge of dehalogenation reactions for synthetic compounds containing chlorine.

- For persistent synthetic compounds, passive transport across cell membranes should be studied, especially the role of cell membranes and serum lipoproteins as transport mediators.

Biological Pollutants

The fourth category of pollutant (discussed in detail in Appendix D) comprises living organisms, which become pollutants when sudden population surges or more widespread distribution have resulted from man's activities. Examples include viruses (which are released to surface waters and the atmosphere by water treatment methods); animal and plant species whose populations have increased because they have been relocated to areas where natural predators are absent; and algae blooms, which occur in nutrient-rich bodies of water.

Living organisms are influenced by the same physicochemical processes as are nonliving substances, but they are unique in several ways. They are living, may be capable of independent movement, and often have shorter lifetimes in the environment than nonliving materials, but maintain their populations through replication. The effects on receptors of exposure to viruses and other small organisms are significant at much lower concentrations because of the capacity for replication.

Enteroviruses (which have been used as the example of Appendix D) move through the environment in a way somewhat modified from that of chemicals, nitrates, mercury, and so forth. In a sense, living processes are superimposed on biogeochemical cycles. Enteroviruses remain viable only for a fairly short time outside a living cell. Depending upon conditions, they may survive from a few days or weeks to several months. During this time their migrations are dependent on natural processes. For instance, viruses may be physically adsorbed onto crevices of particulates, so that aerosols become a mechanism for their dispersal.

If a receptor is not found in time, the virus will die and be degraded. If a proper host is located, replication occurs through the use of the host machinery; new viruses are released to the environment to find a new host, and the cycle starts again. However, the virus cycle differs from chemical cycles in that the former is carried on by newly formed viruses, not by the original infecting agent. Thus, while the same molecule of mercury may migrate throughout the environment, the complete cycling of living organisms involves more than one individual.

To a limited extent, enteroviruses can be stored or accumulated. Virus particles in raw sewage, for instance, may be consumed by a shellfish and remain in its body tissues where replication does not occur; there is some evidence of accumulation of viruses in the tissues.

Specific Recommendations for Viruses

As a result of its considerations of the cycles of viruses, the Panel makes the following observations and recommendations:

- Studies of virus die-off in natural settings and factors contributing to virus inactivation should receive greater emphasis than in the past. The role of bacteria, algae, and other biotic forms in virus inactivation should be characterized, and their significance in natural settings determined.

- In addition to current studies, more information on virus survival and dissemination following spray irrigation or application of sludge or wastewater to land surfaces should be collected. This information should be used in assessing the significance of these practices to public health.

- Studies on virus destruction by disinfectants should be given high priority, in particular basic mechanisms, inactivation kinetics, and the influence of solids-absorbed viruses upon disinfection.

- In view of the continued discharge of waste materials--such as sludges--to lakes, rivers, and oceans, field and laboratory experiments are recommended to evaluate the factors responsible for the persistence of bacteria and viruses in these media.

- In view of a demonstrated bacterial death rate under natural conditions of sunlight, which is one or two orders of magnitude greater than for bacteria in a dark environment, it is recommended that controlled laboratory and field experiments be conducted to quantify the influence of sunlight and other biophysical influences on the survival of bacteria.

- More attention should be directed to determining the role of estuarine sediments as reservoirs of enteric viruses from which induction of a virus carriage status in shellfish may be initiated.

Use of the Cycle Approach for Identification of Needs for Research for Specific Substances

The specific examples presented in Appendixes A, B, C, and D illustrate the cycling approach and the process of identifying research programs by following the cycling of materials. Each Appendix contains a brief survey of existing knowledge in a field covering a class of pollutants, and uses the biogeochemical cycle as a model to identify gaps in knowledge and to list future research needs. In each category, therefore, one substance has been chosen that has a relatively well-studied cycle. The routes, rates, and reservoirs for each of these examples have been detailed to the extent that they are known. A second example has been selected, where appropriate, as a substance about which less is known, and an attempt has been made to show how the better-known cycle can be used to help identify the research most needed for understanding the behavior of the less well-known substance.

The major advantage of the cycling approach is the establishment of a logical scientific basis for extrapolation and research planning; its major limitation is that it cannot predict exactly what will happen for another substance in a similar class. Naive interpretations are a danger. The predictions derived from the cycle approach can be assumed to be true in general, but may not be applicable in a specific location. This is so because the immediate environment (flora, fauna, soil consistency, moisture, pH, available light, presence of other pollutants, and so on) determines specific behavior. Finally, there is a danger in oversimplification, since processes interrelating the cycles of the various elements are very complicated and synergistic effects are poorly understood or unknown. As a result of these limitations, the cycling approach can be recommended as a means for planning the productive research programs, but it is far from being the precise predictive tool that might be desirable as an ultimate goal.

REFERENCES

National Research Council (1977a) Effects of a Polluted Environment: Research and Development Needs. Analytical Studies for the U.S. Environmental Protection Agency. A Report of the Panel on Effects of Ambient Environmental Quality to the Environmental Research Assessment Committee, Environmental Studies Board, Commission on Natural Resources. Washington, D.C.: National Academy of Sciences.

National Research Council (1977b) Research and Development in the Environmental Protection Agency. Analytical Studies for the U.S. Environmental Protection Agency, Volume III. Report of the Environmental Research Assessment Committee, Environmental Studies Board, Commission on Natural Resources. Washington, D.C.: National Academy of Sciences.

National Research Council (1977c) Environmental Impacts of Resources Management: Research and Development Needs. Analytical Studies for the U.S. Environmental Protection Agency. A Report of the Panel on Environmental Impacts of Resources Management to the Environmental Research Assessment Committee, Environmental Studies Board, Commission on Natural Resources. Washington, D.C.: National Academy of Sciences.

National Research Council (1977d) Sources of Residuals and Techniques for their Control: Research and Development Needs. Analytical Studies for the U.S. Environmental Protection Agency. A Report of the Panel on Sources and Control Techniques to the Environmental Research Assessment Committee, Environmental Studies Board, Commission on Natural Resources. Washington, D.C.: National Academy of Sciences.

APPENDIX A

NITROGEN:

AN EXAMPLE OF A NATURALLY-OCCURRING ESSENTIAL ELEMENT

The analysis of biogeochemical cycling of naturally-occurring (biologically) essential substances is well illustrated by nitrogen behavior. Because of its abundance and required links to biological processes, this element's behavior in the environment is one of great importance. In nature, nitrogen compounds are common to all life forms, and are widely found in the land, the sea, and the air. However, as is true of all essential materials, environmental concentrations of certain compounds in excess of natural limits are known to be detrimental to human welfare and ecological processes. Perhaps most important of such compounds are the nitrogen oxides found in the air, water, and soil. As an oxide, nitrogen undergoes a wide variety of physical transport processes in the environment, not only within a single medium, but also between media. The nitrogen oxides are transformed by many different chemical and biological processes into different species. The important similarities (and differences) between nitrogen behavior and sulfur behavior in the environment make these two materials useful for parallel study.

Although much is known qualitatively about the global nitrogen cycle, several important aspects of its behavior remain obscure. One of the major areas of uncertainty is the significance of man's additions of nitrogen compounds to the local environment far in excess of natural conditions. Examples of such additions include NO and NO_2 to the air, and NO_3^- and NH_3 to the soil and water. A variety of pollutants emitted in small quantities may be important, including the amines and organic nitrates or nitrites, and organopesticides containing nitrogen.

The cycle approach offers a useful framework for studying nitrogen substances in the environment, particularly in terms of large-scale emissions superimposed on natural nitrogen oxide levels. Appendix A explores the nitrogen cycle in this light in order to identify environmental research needs. The extrapolation from nitrogen behavior to sulfur behavior is also examined.

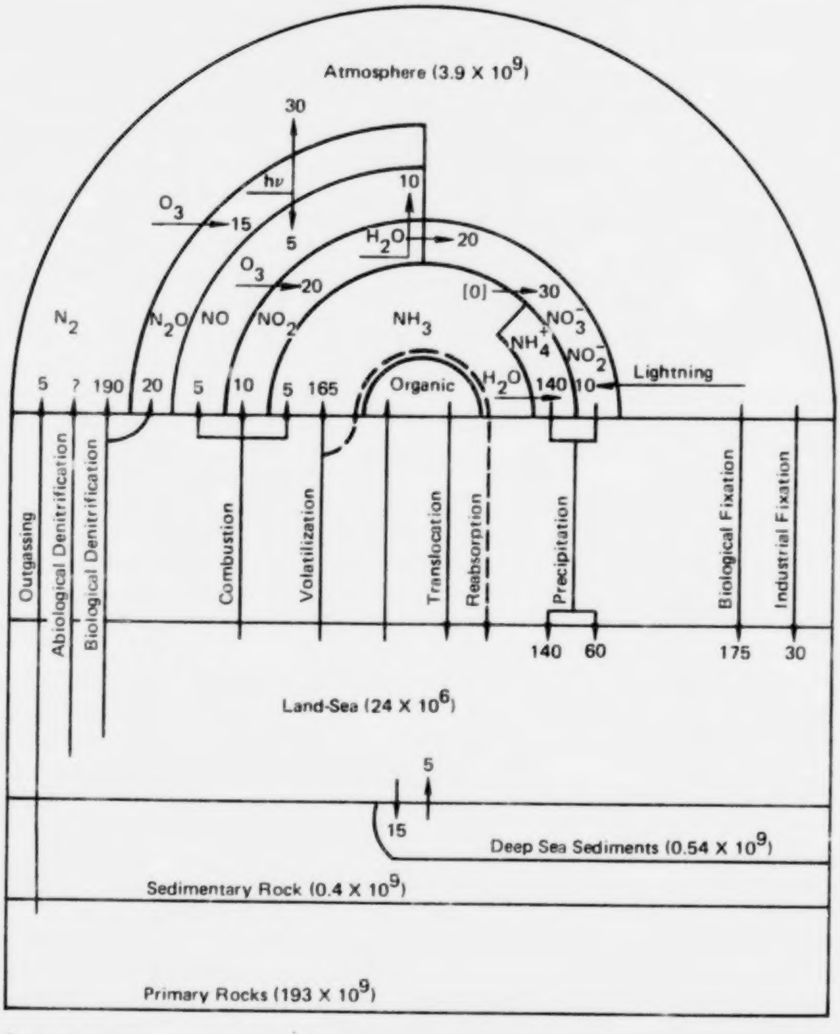
THE GEOCHEMICAL NITROGEN CYCLE

The gross features of the global nitrogen cycle are illustrated in Figure A.1. The principal nitrogen reservoirs are primary rocks and the atmosphere; soil and the hydrosphere hold much less. Nitrogen transfer takes place irreversibly from the primary rocks, but reversibly between the atmosphere, the soil, and natural waters. The main inorganic compounds of interest are NH_4^+, NH_3, N_2, N_2O, NO, NO_2, NO_2^-, and NO_3^-. Current national legislation or guidelines consider only man's contribution to NO_2 (air) and NO_3^- (water) to be pollutants. Organic compounds are identified as a broad class in the cycle, but are not shown as particular species.

As indicated in Figure A.1, major segments of the nitrogen cycle either occur within a single medium or involve interaction between media. Interactions between air and soil, air and water, and water and soil are continuous in nature and serve as the basis for the global nitrogen flow. Transport and transformation processes within media also are essential features of microscale (localized) and macroscale processes. A crucial aspect of the cycle involves rates of transport, or residence times.

Within each medium, certain key processes are important for focusing studies. In the atmosphere, physical transport and chemical transformations are largely dominated on a mass basis by gas phase processes. Suspended colloidal particles are also important features of the atmosphere, but represent a minor interactive component (by mass) in transformation processes. However, in the form of water droplets or ice, such particles may play an important role in transporting nitrogen compounds to the ground. Essentially, no in situ biological processes are known to be significant for nitrogen behavior in the air. In natural waters and in the soil, colloidal particle interactions become an essential and perhaps dominant feature with biochemical processes for nitrogen behavior.

In the following sections, nitrogen behavior by medium is surveyed briefly and areas of significant research needs are identified.


Atmosphere (3.9 X 10⁹)
30
hν
10
O3
15
5
H2O
20
O3
20
[O]
30
N2
N2O
NO
NO2
NH3
NO3⁻
NH4⁺
NO2⁻
Lightning
5
?
190
20
5
10
5
165
Organic
H2O
140
10
Outgassing
Abiological Denitrification
Biological Denitrification
Combustion
Volatilization
Translocation
Reabsorption
Precipitation
Biological Fixation
Industrial Fixation
140
60
175
30
Land-Sea (24 X 10⁶)
5
15
Deep Sea Sediments (0.54 X 10⁹)
Sedimentary Rock (0.4 X 10⁹)
Primary Rocks (193 X 10⁹)

[1] Figures are millions of metric tons. Annual rates are shown for the nitrogen movements and conversions; nitrogen inventory values for the major sinks are shown in parentheses.

SOURCE: Burns and Hardy (1975)

FIGURE A.1 Global Cycling of Nitrogen[1]

ATMOSPHERIC ASPECTS OF THE NITROGEN CYCLE

The nitrogen oxides and ammonia are key trace constituents as condensed material in air. The atmospheric link to the geochemical cycling of nitrogen is shown in Figure A.1. Denitrification is assigned a value of 20 x 10^6 metric tons per year for N_2O and 190 x 10^6 metric tons per year for N_2. With NO_x production from combustion, this is meant to fulfill two key requirements: (1) the atmospheric photochemical conversion to nitrite estimated at 30 x 10^6 metric tons per year, and (2) the combined biological and industrial fixation estimated at 205 x 10^6 metric tons per year. The volatilization of organic nitrogen and ammonia account for the remaining atmospheric nitrogen, which returns to the earth by precipitation or reabsorption. Nitrogen oxides from natural sources of the pedosphere and hydrosphere enter the atmosphere largely in the form of nitrous oxide (N_2O). According to the Burns and Hardy cycle, natural (or quasi-natural) emissions of ammonia are similar to nitrogen emissions, but are significantly larger than emissions from sources of N_2O (Burns and Hardy 1975). Superimposed on natural sources of nitrogen compounds are the anthropogenic emissions, composed mainly of NO and NO_2 from fossil fuel combustion and industrial processing. Agricultural activities may also contribute nitrogen oxide emissions, including some particulate nitrate. Volatilization of organic nitrogen compounds also may be a significant source of atmospheric nitrogen, but both natural and anthropogenic sources of these compounds are poorly characterized at present.

Trace materials may be transported high into the stratosphere, or travel great distances from their original source through the atmosphere. Since the nitrogen oxides are believed to be photochemically active, within days or weeks they will be oxidized or changed by chemical reactions through NO_2 to nitrates. The nitrogen oxides (and products) are removed from the air by absorption at the earth's surface, by aerosol particle formation and particle fallout, or by collection in rain or snow. On a global scale, the removal of nitrogen oxides a few hundred meters above the ground occurs mainly via rain and snow. At ground level, direct gas absorption combined with "dry" aerosol processes are believed to be important (Hidy 1973). Aerosol removal processes include turbulent diffusional deposition and gravitational fallout. Ammonia and the sulfur compounds have been linked to the atmospheric chemistry of nitrogen oxides primarily through aerosol particle chemistry (see Hidy and Burton 1975).

Atmospheric Nitrogen and New Knowledge

By analyzing atmospheric processes in the cycle framework, workers have recognized for some time the highly dynamic behavior of nitrogen oxides in the air. Currently there are four major classes of environmental research that can be derived from examination of the details of the nitrogen cycle. These are: (1) nitrogen fixation chemistry in gases and suspended particles, (2) significance of organic nitrogen compounds in the atmosphere, (3) intermedia flow of nitrogen oxides, and (4) seasonal and geographic characterization of parts of the flow of nitrogen compounds.

Nitrogen Fixation Chemistry

For many years the general link between nitrogen oxides and photochemical oxidant has been known. However, lack of a "complete" nitrogen oxide material balance in air identified with a given airshed has led workers to question whether we have an adequate picture of nitrogen conversion chemistry. Research is now being initiated to examine in detail the less well-measured, less stable nitrogen oxides, including HNO_2, HNO_3, N_2O_5, and NO_3. These molecules are all believed to be present in the atmospheric mixture, and are linked with smog formation. However, their relation to ambient concentrations has not been established, and the kinetics have not been verified (Finlayson and Pitts 1976).

The role of aerosol particle formation and nitrogen oxide transformation has been identified as an uncertain feature of NO_x behavior. The aerosol is known to contain quantities of nitrate that cannot be stable in the condensed phase as nitric acid because of the extreme volatility of this acid. Some researchers believe that the stabilization of nitrate in particles is linked with acid neutralization by ammonia. Thus, the ammonia distribution from natural sources and agricultural activities has become the center of attention in resolving this issue. Measurement of ammonia at atmospheric concentrations is very difficult, and considerable effort is being devoted to development of new instrument techniques for characterization of this gas.

Nitrogen oxides emitted at the ground have a significant bearing on ozone behavior in the troposphere, and there is mounting concern that transport and chemical processes have an impact on stratospheric ozone. Although N_2O is relatively inert in the troposphere, the gas is believed to be transported to the stratosphere and photochemically oxidized, thus influencing the ozone levels at high altitude. A perturbation in soil denitrification resulting in changes in N_2O emissions through extensive nitrate fertilization could have an impact on the stratosphere. The identification of this environmental problem and its subsequent analysis is an application of the cycling approach (Rice and Sze 1976).

Organonitrogen Compounds

While inorganic chemical processes in the atmosphere are reasonably well understood, the origins and transformations of organonitrogen compounds such as the peroxyacetyl nitrate (PAN) series or the nitrosoamines are not. Although concentrations of these materials in the air are low, they may be carcinogenic, and so their behavior requires characterization. Recent analysis of aerosol samples by techniques including high resolution mass spectroscopy has revealed traces of organonitrates and nitrites in particles. Like their gas phase counterparts, the origins of these materials need to be elucidated within the framework of the transport and kinetic approach. To date, few such studies have been initiated.

Intermedia Flow of Nitrogen Oxides

The rates of loss of NO_x to the ground and the release of N_2O from the ground are poorly known, either for soils, vegetation, or natural waters. The transport of nitrate or other nitrogen oxides to the ground with ammonium through acidified precipitation probably influences soils and surface water denitrification in a manner similar to that of current agricultural practice. Acid precipitation has been identified with sulfur as well as nitrate, and increasing problem in the eastern United States.

The transfer of natural materials between the air and the ground now clearly plays an important part in atmospheric chemistry as well as in the chemistry of the pedosphere and hydrosphere. (The term pedosphere was suggested by Friend [1973] to describe the soil-surface rock interactions of the sulfur cycle.) These dynamics require detailed study in future environmental research.

Seasonal and Geographical Variations

Much of the work on geochemical cycles has focused on the global balance of constituents. Localized investigations, which are small-scale analogies to the global approach, provide the structure of studying environmental problems on a region-specific basis. Certainly the highly oxidative, photochemically active atmosphere and dry climate of California present different conditions from humid areas with air of a more "reducing" character. Differences in soil character and vegetation will alter intermedia interactions as well. Although the geographical differences in pollution behavior have been recognized, little effort has been devoted to systematic investigations of variations in rate processes. To plan intelligently for management of environmental controls such work must be undertaken.

Extrapolation to Sulfur

The sulfur transport system parallels and couples with the atmospheric nitrogen cycle. As with nitrogen oxide and ammonia, there are large biologically-related natural sources of hydrogen sulfide (H_2S). Although sulfur dioxide (SO_2) is identified mainly with fuel combustion, significant amounts of SO_2 may come from natural sources such as volcanic eruptions. Particulate sulfate comes directly from sea spray and soil dust, as well as from industrial sources and, to some extent, from fuel combustion. Evidence is accumulating that biogenic emissions of sulfur as H_2S or dimethyl sulfide are oxidized rapidly in the atmosphere to influence sulfate concentrations in some areas of the North American continent (e.g., Hitchcock 1976).

The behavior of nitrogen and sulfur in the atmosphere is similar in many ways, and one system can be used to mirror the other when seeking broad guidelines for productive research. Oxidation reactions of sulfur and nitrogen in the atmosphere are closely related, and are interdependent (Hidy and Burton 1975). The intermedia cycling of nitrogen oxides and sulfur compounds coupled to biogenic processes in natural waters and soils gives similar kinds of atmospheric products. A parallel analysis of biogenic sulfur and nitrogen behavior in the atmosphere recently has been initiated (Rice and Sze 1976, Rice and Nochumson 1977). Organic reactions of sulfur and nitrogen in the atmosphere appear to yield similar oxidized end products, which are toxic in nature. Geographical variability linked to climate, geology, and hydrologic features should be analogous for sulfur and nitrogen compounds.

The analogy between the cycles is far from complete, and the differences between the two elements must be identified by systematic comparisons. These differences must be accounted for in applying the cycling approach to problem identification. Some of these are:

1. Nitrogen oxides in the air play a key role in the formation of photochemical oxidants, while sulfur oxides do not.

2. Unlike the volatile nitrous and nitric acids, sulfuric acid occurs in the condensed phase in the range of micrograms ($\mu g/m^3$) concentrations.

3. Because of the influence of NH_3 on the volatility of HNO_3, ammonia appears to be more important to the kinetics of nitrate formation than to that of sulfates.

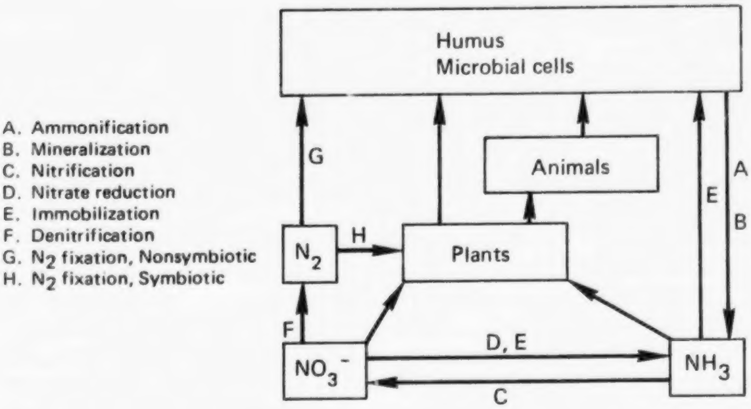
4. Products of organic sulfur or nitrogen reactions in the atmosphere are likely to be similar, but the (identified) organonitrogen oxides appear to exist in significantly larger concentrations than organic sulfur oxide compounds, particularly in photochemical smog.

These important differences in the behavior of atmospheric nitrogen and sulfur clearly indicate that extrapolation must be done intelligently and with care. Nevertheless, a knowledge of the physical transport and chemical transformation of nitrogen has been important in the development of research priorities for atmospheric sulfur. Many of the processes are so closely linked that they should be studied in unison. In fact, a major study of aerosol behavior in Los Angeles was undertaken recently on this basis (Hidy 1974).

THE NITROGEN CYCLE AND THE PEDOSPHERE

The atmospheric portion of the geochemical nitrogen cycle is closely coupled with the pedosphere and the hydrosphere. Like the atmosphere, the latter two in themselves have unique features of cycling that place great emphasis on biochemical processes and the chemistry associated with solids and liquids.

Probably the greatest variety of transformations of nitrogen occur in the soil. Alexander (1961) has developed the very general model of the terrestrial nitrogen cycle shown in Figure A.2. While the atmospheric transport and transformations of nitrogen are largely physical and inorganically chemical, the reactions of nitrogen in soils occur primarily as the result of metabolic processes. Nitrogen is incorporated into biologically important compounds largely from three inorganic compounds: nitrogen gas (N_2), ammonia (NH_3), and nitrate ion (NO_3^-). Each of these forms may be absorbed directly from the atmosphere or water at their interface with soil.


Humus
Microbial cells
A. Ammonification
B. Mineralization
C. Nitrification
D. Nitrate reduction
E. Immobilization
F. Denitrification
G. N_2 fixation, Nonsymbiotic
H. N_2 fixation, Symbiotic
G
Animals
A
E
B
H
N_2
Plants
F
D, E
NO_3^-
NH_3
C

SOURCE: Alexander (1961), Alexander, M. (1961). Introduction to Soil Microbiology. New York: John Wiley and Sons.

FIGURE A.2 General model of the terrestrial nitrogen cycle.

Figure A.2 also illustrates that the predominant flow of NH_3, N_2, and NO_3^- is toward microbial cells and that a major sink is in humic material. The flow may be quite direct as in the case of immobilization of ammonia by soils, or very indirect as in the case of uptake of nitrates by plants followed by animal consumption and eventual decomposition of the animal tissue. The cycling of this nutrient is completed by the eventual conversions of humic material back to ammonia. Since this is essentially the only biological means for releasing nitrogen from humic material, the mineralization processes involved, i.e., decomposition, ammonification, and nitrification, are vitally important to the continual cycling of nitrogen in the environment.

The amount of nitrate in the soil is largely dependent upon the rates at which the following important reactions take place: nitrification and denitrification, immobilization, plant and animal uptake, addition of nitrogen to soil or water by the activities of man and nature, and leaching and runoff. Each of these broad categories has been studied in some detail and much is known about the quantitative and qualitative aspects in relation to nitrate pollution; however, there are many gaps in the data characterizing such changes.

Gaps in Current Knowledge

Analysis of the nitrogen cycle in the soil indicates several areas in which research is needed. Some key topics include:

1. Role of the biotic processes in nitrogen speciation and its flow in the geochemical cycle.

2. The relationship of the physical, chemical, and microbial properties of soil to the rate of nitrate leaching, runoff, denitrification, production, and transformation.

3. The influence of certain natural and man-made factors on nitrate production, transport, and transformation in soil. Included are such factors as geologic and hydrologic features, and cultural practices such as irrigation, conservation, cultivation, and fertilization.

4. The influence on nitrate movements in soil of natural seasonal, annual, and geographic variations in climate.

5. The comparative reliability of data obtained from laboratory, greenhouse, lysimeter, and field studies; also the accuracy with which data may be transferred from one location to another on the basis of knowledge obtained from soil surveys.

6. The dynamic character of the origin, concentration, and movement of molecular nitrogen and nitrogen oxides in and out of the solum.

The biota plays a key role in the storage, transfer, and transformation of nitrogen in the soil-atmosphere-hydrosphere continuum. The biological aspects of the soil environment need study in order to estimate more accurately the amount of nitrogen present in the biota in relation to that residing in the air and water. Also, estimates of the rate of flow between these cycle components must be improved.

The diverse physicochemical properties of soils in the presence of living systems, especially microbes, provide an extremely complicated set of variables to systematize in evaluating pollution impact. These variables must be investigated in broad classes. Thomas (1970), for example, maintains that there are four physical properties of soils that affect the mobility of salts at least as much as do any of the chemical properties. These are: capillary conductivity of drying soil, soil water content, pore size heterogeneity, and presence of a water table or zones restricting movement of water. Of all the research in this area that requires emphasis, investigations of soil-water-solute relations under variable climates is the most pressing.

Our knowledge of the influence of soil modification or treatment through natural processes or man's activities on a geographically specific basis is not adequate enough to permit the characterization of nitrogen flow. Systematic long-term studies on test ground must be undertaken at geographically representative locations to first determine the rates of natural storage or migration of nitrate in soils and soil water as a function of time of year. These experiments should be followed by stepwise investigation of the influence of disturbances related to current agricultural practices.

The following approaches to evaluating the impact of nitrate on the environment have been suggested by Nelson (1970). They emphasize the need for in situ, interdisciplinary studies on areas that are manageable in size.

1. Small watersheds with limited sources of nutrients should be selected in which there is neither surface runoff nor underground flow originating from outside the watershed, and where ground waters collected from the watersheds are not lost before reaching the gauging and sampling stations. Studies may be done on single or on paired watersheds.

2. Tile drained plots equipped with runoff sampling equipment should be used to study the flow of nitrogen compounds through level or irrigated lands.

3. Soil samples under fertilized and unfertilized lands should be taken at various depths down to the water table or bedrock to give strong evidence of nitrate in transit. These studies should be coupled with water samples extracted from core holes or groundwater wells.

4. Data on nutrient loss due to surface runoff should be collected from fertilized and unfertilized plots under natural field conditions or with rain simulators.

These studies should be planned so that they cover annual and seasonal behavior. In addition, the design must be broad enough to incorporate intercomparison experiments between laboratory or greenhouse approaches and field programs. In such programs workers must be convinced that segments of the soil ecological system can be isolated and investigated meaningfully within the total system.

Extrapolation to Sulfur

The rate at which sulfur and nitrogen compounds are transformed in the environment depends upon essentially the same physical, chemical, and biological factors. Research approaches, such as using paired watersheds, runoff plots, soil profile sampling, and so on, are also essentially the same.

The extrapolation and transfers of knowledge from studies on nitrates to needed programs on sulfates do not stop here. A thorough understanding of nitrogen and its transformations in the soil can be helpful in studying the changes that certain other elements undergo in the same environment. In the case of sulfur, extrapolations are possible and valuable because many similarities exist, some of which are noted below:

1. The rates at which both sulfur and nitrogen compounds are transformed in the soil depends upon the same basic variables, such as moisture, aeration, temperature, pH, structure, and texture.

2. Both elements are constituents of plant and animal protoplasm.

3. Both occur in organic and inorganic form in the soil; the greater portion of each is in organic combination. The transformation of both depends heavily on soil organisms.

4. There are certain similarities that exist in the oxidation of compounds of sulfur and nitrogen.

5. Conditions necessary for the reduction of nitrate and sulfate are very similar.

6. Both elements are important in amino acid and protein synthesis.

7. Sulfur and nitrogen form strong acids in the soil.

8. Laboratory and field research techniques necessary to quantify their movements and magnitude in the soil are essentially the same.

9. There are also other physiological and biochemical similarities in plants and animals.

Striking differences also occur between these two elements per se and in relation to their movement in the environment. Herein lies the potential for separate, new research endeavors in order to explain fully the environmental impact of sulfur. For example, in studying sulfur, one must consider some of the following ways in which it differs from nitrogen:

1. Elemental sulfur may occur as a solid in the soil.

2. Sulfur cannot escape to the atmosphere as a gas in the elemental form; neither can it be fixed from the air by symbiotic or nonsymbiotic organisms.

3. Sulfur, although essential to plant and animal growth, does not occur in all amino acids.

4. The atmosphere and soil air contain minute quantities of sulfur in contrast to nitrogen.

5. Sulfur is required in much smaller quantities than nitrogen for normal plant growth.

6. Soluble sulfur compounds, especially sulfates, move freely in the soil compared to some nitrogen compounds, e.g., ammonium.

7. Sulfur compounds have not been implicated to any significant extent in eutrophication; therefore, their movement through soil to ground water, lakes, and streams to date has not been of great concern.

Many other similarities and differences could be mentioned. It is apparent, however, that a thorough comprehension of nitrogen and its tranformations in the soil facilitates an understanding of sulfur and its transformations. Should sulfur also become a concern from a pollution standpoint, potentially successful research approaches could quickly be outlined by a recognition of the differences between the two elements.

Much more rapid progress on understanding the fate of pollutants in the environment can be made if, first, similar pollutants are grouped on the basis of specific properties and, second, if applicable data are transferred and extrapolations are made from one compound (or organism) to another, thereby expediting the third step, the search for new information by the research process.

AQUATIC ASPECTS OF THE NITROGEN CYCLE

The third major segment of the nitrogen cycle takes place in the hydrosphere.

Bacterial nitrification and algal assimilation of nutrients are important in the natural cycling of nutrient materials in natural waterways. The first process oxidizes ammonia to nitrite and nitrate compounds. In the second process, algae convert inorganic substances to organic ones, parts of which are hydrolyzed to form ammonia.

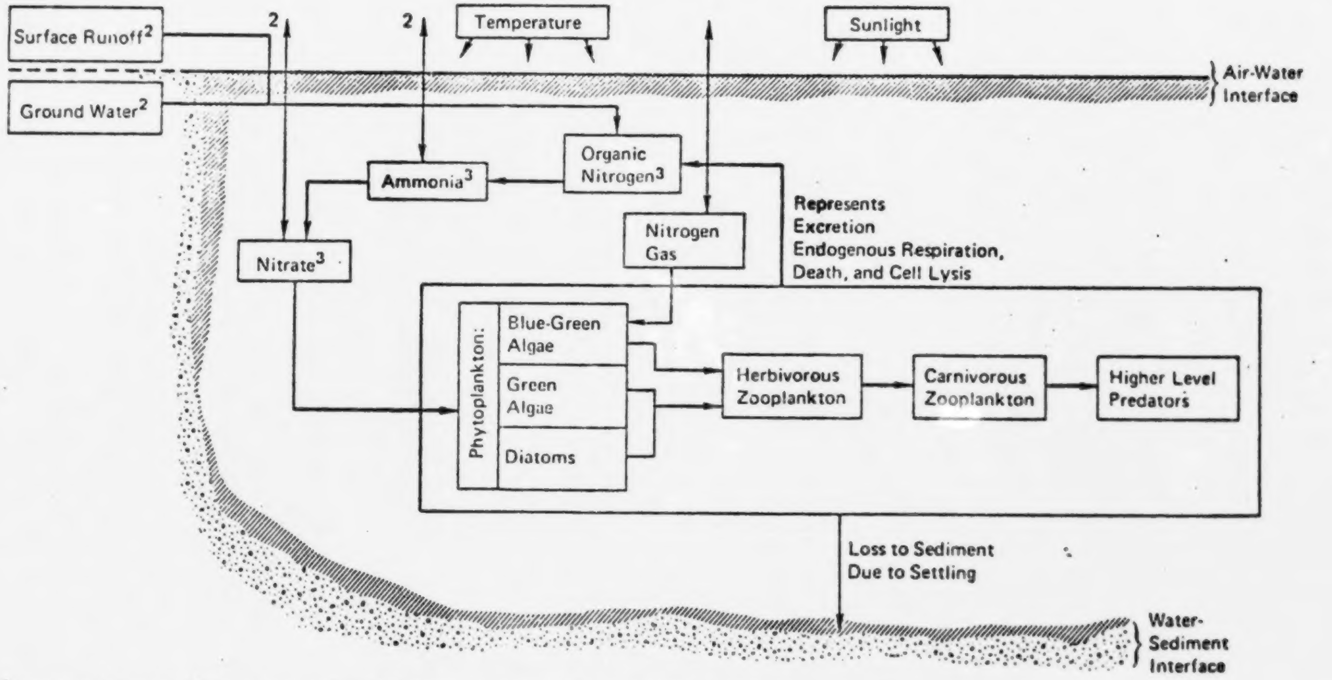
Physical processes are of secondary importance to chemical and biological changes in the aqueous environment. Transport takes place by water flow, which can be localized or can involve extensive distances. Sediment settling, which is a means for removal of nutrients, is the most important physical process. Others are sunlight and temperature. The depth to which light penetrates a given body of water will have a significant influence on the phytoplankton population, and hence on all other organisms present.

A summary of the nitrogen cycle within the aquatic environment is depicted in Figure A.3. Each arrow represents both a transformation and the rate at which the transformation occurs. The values for these rates are known empirically, but not fundamentally.

The bacterial processes are shown in the upper left hand side of the diagram, while assimilation of nitrogen compounds by algae and higher organisms are presented in the lower right. Each step represents hydrolysis, oxidation, reduction, predation, or decay. External inflows of energy (e.g., temperature, sunlight) drive the ecosystem.

Ammonia (NH_3) is oxidized under aerobic conditions to nitrite (NO_2^-) by bacteria of the genus Nitrosomonas. The nitrite thus formed is subsequently oxidized to nitrate (NO_3^-) by bacteria of the genus Nitrobacter.

If the numbers of bacteria are limited, the concentration of the bacteria appears to be the primary control on the rate of nitrification, with the concentration of ammonia having a secondary effect. If there is an ample supply of bacteria, however, the rate appears to be controlled by the concentration of ammonia. The total number of nitrifying agents is related to the generation time of the organisms.


Surface Runoff²
Ground Water²
2
2
Temperature
Sunlight
Air-Water Interface
Organic Nitrogen³
Ammonia³
Nitrate³
Nitrogen Gas
Represents Excretion Endogenous Respiration, Death, and Cell Lysis
Phytoplankton:
Blue-Green Algae
Green Algae
Diatoms
Herbivorous Zooplankton
Carnivorous Zooplankton
Higher Level Predators
Loss to Sediment Due to Settling
Water-Sediment Interface

[1] In order to focus on the nitrogen cycle, the parallel and essential cycling of phosphorus has been omitted.
[2] These sites also represent discharges from anthropogenic sources.
[3] The conversions of organic nitrogen to nitrate are bacterial processes.

FIGURE A.3 Transport and Transformations of Nitrogen and Nitrogen Compounds in Water

The common source of nitrifying bacteria is soil, where they are usually found in abundance. Their numbers in sewage are low, but increase through biological treatment to an order of 1000/ml. In rivers receiving wastewaters, nitrifying bacteria are present to varying extents, depending on the nature and treatment of the effluents and the characteristics of the drainage area. A natural habitat is biological aggregates or certain surfaces apppropriate for optimum growth and accelerated metabolism.

Under conditions of low or zero dissolved oxygen, a great variety of bacteria are capable of denitrification. This process involves bacterial reduction of nitrate to nitrite and then to nitrogen gas, although complete reduction to ammonia may also occur under special circumstances. The nitrate and nitrite compounds in these reactions serve as an oxygen source for the bacteria without drawing on the dissolved oxygen resources of the water body.

Algae assimilate both ammonia and nitrate into cellular protoplasm. This process is reversible during respiration: i.e., cellular protoplasm may also be converted to ammonia and nitrate (respiration). The forward reaction, an integral part of algal growth (production), determines the extent to which algal biomass is produced. The energy for this biomass production is gained from photosynthesis. The reverse reaction (respiration) involves the use of protoplasm for energy and the decay of the biomass to inorganic and stable organic forms. The balance between assimilation and respiration is crucial to the oxygen content as well as to the food web of the water body.

If nutrient concentrations are large and other conditions favorable, the forward reaction will dominate and produce a large algal biomass. Algae are the food source on which the entire aquatic food web depends. Herbivorous zooplankton and other higher animals graze on algae, and fish feed on the zooplankton.

If algal growth is excessive, the subsequent destruction and decay of the biomass consumes critical dissolved oxygen supplies in the water. It is the decay and the microbial degradation of this biomass that eventually recycles ammonia to begin the cycle again.

Gaps in Current Knowledge

Although much has been done to quantify the rates of each step described in the previous sections, many significant questions remain unanswered. Areas of uncertainty include:

1. The exchange between the bed and the water column, and the effect of aerobic and anaerobic conditions on the rate of exchange. This factor is of particular significance in lakes, where sedimentation of the various components from water to sediment is usually important.

2. The delineation of the transformation of nutrients by generic groups of phytoplankton. Current analyses lump all species into three or four major groups, but this system must be refined so that subgroups are denoted according to water use. For instance, at the microscopic level, studies should be conducted to determine the separate activities of diatoms and green and blue-green algae.

3. The degree and manner in which nutrients become available to growth of the phytoplankton and periphyton. While many municipal, industrial, and agricultural effluents discharge varying amounts of nutrients, those nutrients contained in runoff may be less readily available depending on the nature of the material to which they are attached or bound. The time scale of the release of the nutrients is of key importance.

4. As our fundamental understanding and quantitative descriptions of the food chain become more complete and useful, research on the accumulation of toxic substances in the various stages should be appropriately phased into research projections This step, of necessity, combines the relevant phenomena, as briefly described in this section, with those discussed under the categories of the synthetic chemicals and toxic metals.

The Problem of Eutrophication

An understanding of the transforming mechanisms that characterize the various geochemical and biophysical cycles of nitrogen and its compounds is important in order to understand the problems that occur when these compounds are discharged as a result of anthropogenic activities. The discharge of nitrogen and phosphorus from both point sources, (e.g., treatment plants) and distributed sources (e.g., runoff from developed, agricultural, and urban areas) contribute to eutrophication.

Effluents from secondary and tertiary waste treatment plants contain dissolved, colloidal, and suspended solids in both the organic and inorganic forms. The nature of these organic solids, which may be bacterial cells and/or less readily oxidizable compounds, should be studied more thoroughly. More important, the concentrated residues in sludges, both treated and untreated, should receive greater attention. The residuals from advanced treatment of wastewaters, and the sludges resulting from this treatment, should be studied more thoroughly through detailed measurements and evaluations in order to provide a basis for the understanding of their decay and transformations in natural water systems.

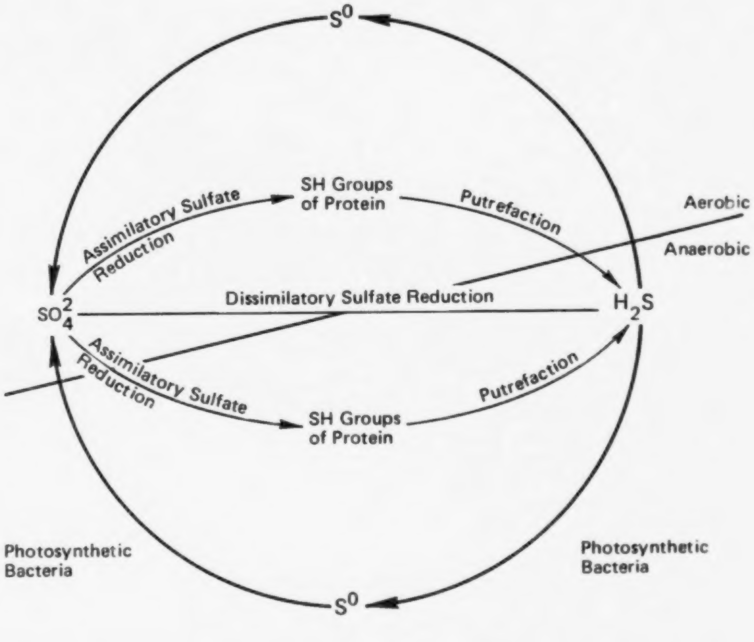
These liquid effluents and sludges contain varying amounts of nutrients, particularly ammonia. The assimilation of ammonia by bacteria and algae is a critical step in the process of eutrophication. It is not known whether initial assimilation of excess ammonia is primarily bacterial or algal. If bacterial uptake predominates, the one-day to one-week lag time before the transferral of nitrate to algae tends to minimize the potential for eutrophication. If an algal assimilation of ammonia predominates, the potential for eutrophication increases.

Extrapolation to Sulfur

The sulfur-nitrogen analogy developed for the air and soil media can be carried through for water to present a complete picture of the cycling perspective. There are both natural and man-made sources of sulfur and its compounds. Like nitrate, sulfate is present in rain water and it is also contained in sedimentary rocks, from which it may be released by oxidation. Therefore, most natural waters contain some concentration of sulfate. On the other hand, whereas anthropogenic nitrogen in water comes from agricultural practice, metal mining processes and pulp and paper processes to a more limited degree are the primary industrial sources of discharges of sulfur to waterways.

Sulfate is one of the more common anions in water. It is present in fresh water in varying degrees and in relatively high concentrations in seawater. The chemical transformations of sulfur are similar in many ways to those of nitrogen. Sulfate can be formed by oxidation of hydrogen sulfide under aerobic conditions or through biochemical processes under anaerobic conditions. Most microorganisms and plants can use sulfate as their sole source of sulfur, converting it into organic sulfhydryl compounds. Decomposition of organic sulfur-containing compounds by microorganisms produces hydrogen sulfide. This is analogous to ammonia production, and to H_2O release. Production of H_2S is an important process in the freshwater environment, where the concentration of the sulfate ion is usually low. On the other hand, sulfate reduction by organisms, another route to the formation of H_2S, is probably the most important means of its production in the sea. Hydrogen sulfide oxidizes rapidly to elemental sulfur and finally to sulfate through the sulfur-oxidizing bacteria under aerobic conditions. If light is available, H_2S can also be oxidized anaerobically by photosynthetic bacteria. These processes complete the sulfur cycle as shown in Figure A.4.

When sulfur-oxidizing organisms convert H_2S into sulfuric acid, a marked drop in pH results. In coal-mining regions, oxidation of H_2S leads to the formation of sulfuric acid, which leaches into the surrounding streams. A significant water quality problem arises because of these low pH waters. It is expected that the sulfur cycle has a significant bearing on the control of acid production in these waters.


S0
SH Groups of Protein
Assimilatory Sulfate Reduction
Putrefaction
Aerobic
Anaerobic
SO4 2
Dissimilatory Sulfate Reduction
H2S
Assimilatory Sulfate Reduction
Putrefaction
SH Groups of Protein
Photosynthetic Bacteria
Photosynthetic Bacteria
S0

SOURCE: Thomas (1970). Thomas D. Brock, Biology of Microorganisms, copyright 1970, p. 471. Reprinted by permission of Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

FIGURE A.4 Schematic diagram of sulfur fixation in aqueous systems.

The H_2S newly formed via reduction of sulfate by anaerobic bacteria may act as an agent to reduce metal ions. When anaerobic conditions occur in natural waters, the iron in the sediment--usually present in the ferric form--is reduced to the ferrous form by H_2S. Other compounds that are reduced along with the iron are of equal and frequently greater importance. Phosphorus precipitated with iron complexes is readily released into the solution. The amount of this nutrient stored in the sediments is one of the most important considerations in the eutrophication problem of natural waters.

REFERENCES

Alexander, M. (1961) Introduction to Soil Microbiology. New York: John Wiley and Sons.

Brock, T. D. (1970) Biology of Microorganisms. Englewood Cliffs, N.J.: Prentice-Hall.

Burns, R.C. and R.W.F. Hardy (1975) Nitrogen Fixation in Bacteria and Higher Plants. New York: Springer-Verlag.

Finlayson, B.J. and J.N. Pitts, Jr. (1976) Photochemistry of the polluted troposphere. Science 192(4235):111-119.

Friend, J. (1973) The global sulfur cycle. Pages 177-201, Chemistry of the Lower Atmosphere, edited by S.I. Rasool. New York: Plenum Press.

Hidy, G.M. (1973) Removal processes of gaseous and particulate pollutants. Pages 121-133, Chemistry of the Lower Atmosphere, edited by S.I. Rasool. New York: Plenum Press.

Hidy, G.M. (1974) Characterization of Aerosol in California (ACHEX). 4 Volumes. Final Report of California Air Resources Board, by Rockwell International Science Center. Volumes I and III. Sacramento, Calif.: California Air Resources Board; Volumes II and IV, PB-248 799 and PB-247 947. Springfield, Va.: National Technical Information Service.

Hidy G.M. and C.S. Burton (1975) Atmospheric Aerosol Formations by Chemical Reactions. Proceedings of the Symposium for Chemical Data for Upper and Lower Atmosphere. Journal of Chemical Kinetics Symposium No. 1. New York: John Wiley.

Hitchcock, D. (1976) Atmospheric sulfates from biological sources. Journal of the Air Pollution Control Association 26:210-215.

Nelson, L.B. (1970) Research needed to resolve the plant nutrient-water quality issues. Pages 75-81, Nutrient Mobility in Soils: Accumulation and Losses, edited by O. P. Englestad. Special Publication No. 4. Madison, Wis.: Soil Science Society of America.

Rice, H. and D.L. Nochumson (1977) Association of sulfur emissions and observed sulfate occurrences. Chapter 3, Perspective on the Current Airborne Sulfate Problem. Final Report. Volume 1. Prepared for the American Petroleum Institute TF406-76T. Westlake, Calif.: Environmental Research and Technology, Inc.

Rice, H. and N.D. Sze (1976) Nitrogen cycle factors contributing to N_2O production from fertilizers. Geophysical Research Letters 3:343.

Thomas, G.W. (1970) Soil and climatic factors which affect nutrient mobility. Pages 1-20, Nutrition Mobility in Soils: Accumulation and Losses, edited by O.P. Engelstad. Special Publication No. 4. Madison, Wis.: Soil Science Society of America.

BIBLIOGRAPHY

Brady, N.C. (1974) The Nature and Properties of Soils. 8th Edition. New York: MacMillan.

APPENDIX B

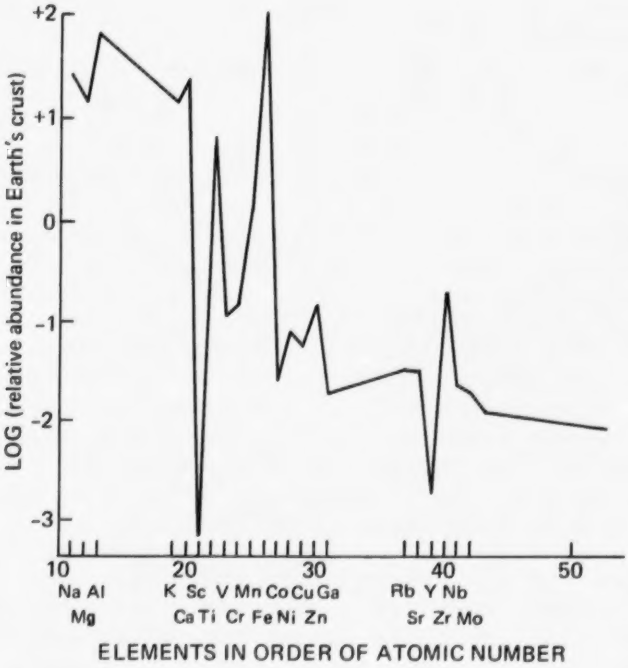
HEAVY METALS:

EXAMPLES OF NATURALLY-OCCURRING NONESSENTIAL ELEMENTS

INTRODUCTION

Before organic matter evolved into living systems on this planet, a number of inorganic equilibria existed, which were influenced by the various physical constraints on the earth. Upon this matrix of inorganic compounds, evolution led to the synthesis of both coordination complexes and organometallic complexes. Initially, metal-ligand interactions occurred in a strictly anaerobic environment. Many primitive coordination complexes still exist; for example, the ferredoxins represent electron transfer proteins designed on a system of solubilizing, by protein association, the otherwise insoluble iron-sulfide complex. Later, molecules of more adaptable design evolved that could function in a variety of catalytic processes. One example of such a molecule is DNA-polymerase, which has a zinc atom at its active site; another is the iron complex heme, which initially evolved to facilitate the reduction of soluble inorganic ions such as sulfate and nitrate. The appearance of molecular oxygen in the biosphere led to the evolution of heme complexes that could function in the reduction of oxygen to water. This reaction clearly served as a detoxification mechanism, because molecular oxygen is exceedingly toxic to the anaerobic bacteria. The scene was thus set for the evolution of complexes that deal with toxic elements and so give populations of organisms selective advantages. The environment is critical to the survival of the cell, and, fortunately, the initial inorganic matrix in the earth's crust directed evolution toward natural biogeochemical cycles for all elements, including toxic ones. We are dealing with natural biological cycles, and therefore should not be surprised to find inorganic and organometallic equilibria for toxic elements in aqueous systems.

There is a very delicate balance between the use of metals for important catalytic processes that occur in cells of higher organisms and the bioaccumulation of metals to a toxic level. This balance is not only affected by the availability and abundance of metals in the earth's crust, but also by microbial interconversions of metals to coordination and organometallic complexes in the environment. Figure B.1 indicates the correlation between biological availability of essential metals and their abundance in the earth's crust. Those metals with an atomic number below 40 are most abundant. All other metals can be regarded as trace elements, with the exception of tin and barium.



SOURCE: Wood (1975)

FIGURE B.1 Abundance of Metals in the Earth's Crust

Of the metals presented in Figure B.1, scandium is a trace metal, and titanium and aluminum are virtually unavailable for bioaccumulation because they form hydroxides that are very insoluble in water. Nickel and chromium are rarely found in significant concentrations inside cells; they are made biologically unavailable by their formation of stable octahedral complexes with silicates in the soil. This process of elimination shows that few metals are available, and even fewer are directly involved in biocatalysis. Besides sodium (Na^+) and potassium (K^+), which play very critical roles, only 11 other metals have been shown to be involved in important catalytic reactions in the cell. These metals either function at the active sites of enzymes or regulate enzyme activity. Typical reactions catalyzed by metalloenzymes include oxidation/reduction, hydration and dehydration, hydrolysis, or the reverse of aldol condensation. In order of abundance we find that, in the metalloenzymes discovered to date by biochemists, the following metals rank

$$Fe > Mg, Mn > Ca > Zn > Cu > Co > Mo > Ni > V > Cd.$$

Metals of biological concern can be conveniently divided into three groups: (1) light metals, or those that are usually transported as mobile cations in aqueous solution (e.g., Na^+ and K^+); (2) transition metals, or those that are essential in catalysis and may be toxic in high concentrations (e.g., Fe, Co, Cu, Mo); and (3) heavy metals and metalloids, or those that may be required as trace elements by the cell, but which at low concentrations are toxic to the cell (e.g., Hg, Pt, Au, Pd, Sn, Be, As, Se, Te).

Table B.1 classifies elements in terms of their relative toxicity and availability. Biologists should give careful consideration to those metals in category B. Category C deserves notice as well, because insoluble toxic elements can be rendered soluble by man-made chelating agents such as polyphosphates and nitrilotriacetic acid (NTA), both of which are added to our water supply in detergents. For example, the very toxic lanthanides will complex with polyphosphate or NTA thereby making them available to biological systems.

Toxic metals that form organometallic compounds, especially the metalalkyls (e.g., methylmercury), deserve special concern since most metalalkyls accumulate in cells

TABLE B.1 Classification of Elements According to their Toxicity[1]

A	B	C
Noncritical	Very toxic and relatively accessible	Toxic but very insoluble or very rare
Na	Be	Ti
K	Co	Hf
Mg	Ni	Zr
Ca	Cu	W
H	Zn	Nb
O	Sn[4]	Ta
N	As[4]	Re
C	Se[4]	Ga
P	Te[4]	La[3]
Fe	Pd[4]	Os
S	Ag	Rh
Cl	Cd	Ir
Br	Pt[4]	Ru
F[2]	Au[4]	Ba
Li	Hg[4]	
Rb	Tl[4]	
Sr	Pb[4]	
Al	Sb	
Si	Bi	

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1. Elements omitted from this table should not be neglected in the environmental sense. For example, iodine and manganese are important elements, but they fit more than one category for the above classification.

2. Some may argue with this designation, but we do add fluoride to drinking water.

3. All the lanthanides are very insoluble and some are very rare.

4. Metals having metal alkyls which are stable in aqueous systems which have been reported to be biomethylated.

SOURCE: Wood (1974) Biological Cycles for Elements in the Environment, Wood, J.M. Science Vol. 183, pp. 1049-1052, Table 1, 15 March 1974. Copyright 1974 by the American Association for the Advancement of Science.

and are poisonous to the central nervous systems of higher organisms. Metalalkyls that are stable in water and can be synthesized either chemically or biochemically include the following toxic elements: Hg, Sn, As, Se, Te, Pd, Pt, Au, Tl, and Pb.

Mercury, lead, and cadmium are metals of the greatest concern because of their high toxicity and wide dispersal in the environment. The case of mercury pollution has clearly demonstrated the profound importance of understanding biologically-mediated transformation reactions that yield metal-organic compounds with a high potential for bioaccumulation and toxicity. It has also illustrated the value of fundamental information on physical-chemical states of an element (vapor, aqueous, liquid, solids), its association-dissociation reaction, oxidation-reduction processes [Hg(II), Hg(I), and Hg^0], adsorption of molecules and ions in solution, and distribution equilibria between phases (biota, sediments, minerals). Experience with mercury on a global level has clarified the importance of its physical-chemical properties in the cycling of the element through the air-water-land system. Under natural, or "pre-man" conditions, mercury vapor is a key species in the geochemical cycle of mercury through the atmospheric, oceanic, and soil reservoirs. Present-day mining and industrial emissions have resulted in high flux rates of mercury through the environment. It is estimated that man's activities have increased the flow of mercury from the land to the oceans via rivers almost fourfold (Garrels et al. 1975). On a planetary basis, the mercury cycle is now more clearly understood as far as the relative contributions of vaporization of elemental mercury from the land and oceans, man-caused emissions, rainout, river transport, and oceanic sedimentation are concerned. On a local, regional, or ecosystem basis (rivers, lakes, coastal environments, soils), the potential rate-determining role of biomethylation of mercury is now recognized, although few predictive models are available; we have but limited information on actual methylation and degradation rates under specific environmental conditions.

Experience with the mercury cycle can be extrapolated to other metals, and these can immediately be separated into metals that are capable of forming stable metal alkyls and those that are not. For example, methyl-B_{12} is an environmentally important molecule because it can react with a number of metal ions or salts of metalloids (such as arsenic and selenium) to produce metal-alkyls that bioaccumulate in the central nervous system of higher organisms. Column B in Table B.1 contains toxic elements that react with methyl-B_{12}. The chemical properties of some of these are discussed below.

THE GEOCHEMISTRY OF TOXIC ELEMENTS

To understand the movement of toxic elements in geochemical cycles, it is necessary to examine several factors. Chemical speciation must be determined by distinguishing the chemical species in solution, colloidal, and particulate phases. In addition, the following studies are critical: (a) ion association; (b) dissociation in fresh water and seawater; (c) oxidation-reduction reactions (where they exist); and (d) distribution of chemicals between solution and solid phases by adsorption-desorption, precipitation-dissolution ion exchange processes, and volatilization. The importance of speciation cannot be overemphasized; chemical behavior of any element in the environment depends on its form. A geochemical approach that considers various environmental reservoirs and rates of exchange between them provides information on the overall fate of pollutants; the sources and geographical location of toxic elements are also important, especially in relation to the movement of toxic elements caused by man's activities.

Jernelov (1974) presents a comprehensive set of environmental characteristics and properties that, when determined, permit an evaluation of potentially undesirable inputs. They are briefly summarized as follows: (a) production and emission in relation to natural flux, (b) residence times in various reservoirs, (c) bioaccumulation, both "passive" and "active", (d) physical and chemical properties relating to dispersion (e.g., volatility, adsorption tendencies, dissociation-association reaction, formation of insoluble precipitates), (e) toxicity to aquatic organisms, (f) toxicity to man and other mammals, (g) long-term biological effects on ecosystem metabolism, and (h) transformation reactions by organisms. Jernelov's monograph examines selected toxic elements in detail. The periodic table is a guide to certain general features pertinent to the chemical properties of toxic elements. In the discussion that follows here, mercury and cadmium have been chosen as examples of toxic metals that bioaccumulate by entirely different mechanisms.

CHEMICAL SPECIES OF MERCURY AND CADMIUM IN THE BIOSPHERE

Cadmium is a IIB metal (atomic number 48, atomic weight 112.4) in the periodic table of the elements. In aqueous systems it exists only in the elemental form and in the two-valence state, Cd(II). Zinc and mercury are also IIB metals. Zinc, like cadmium, is limited to the two-valence state, but mercury can exist as mercurous ion, in the Hg(I) oxidation state, or as Hg(II).

Disproportionation of mercury is extremely pertinent to its global distribution, i.e.,

$$Hg_2^{2+} \longleftrightarrow Hg^{2+} + Hg^0$$

The vapor pressure of mercury metal establishes steady-state concentrations of mercury in the air, water, and at the earth's surface. The geochemical equilibrium can be perturbed by biological reduction of mercuric salts to mercury metal, which will be subsequently lost to the water and to the atmosphere.

Cadmium, zinc, and mercury are classed among the B-metal cations with respect to their coordination tendencies with the donor atoms of various ligands. The B-metal cations are distinguished by an outer shell of 18 electrons; they are highly polarized and are described as "soft-sphere" cations. Among the B-metal cations are Zn(II), Hg(I), Hg(II), Ag(I), Cu(I), and Pb(II). The B-metal cations tend to interact with ligands by covalent bonding, i.e., sharing of electron pairs, rather than through coulombic forces. When bonding, the B-metal cations tend to take up electrons (Lewis acidity) and the ligand atoms tend to give them up. Thus, Cd(II) tends to form stable precipitates and complexes with donor atoms and ions of low electronegativity, such as sulfur, iodine, chlorine, nitrogen, selenium, bromine, and phosphorus. Covalent bonding tendency is quite weak with oxygen and fluorine.

Coulombic forces are dominant in the bonding of A-metal cations, such as Ca(II), Mg(II), Be(II), Ba(II), and Al(III). These metal ions tend to bond strongly to oxygen, H_2O, OH^-, CO_3^{-2}, carboxylic acids, aminopolycarboxylic acids, and phosphates. For the A-metal cations, coulombic factors such as the charge of the cation, the charge of the ligand, and the radius of the cation are paramount in determining affinities between the metals and ligands. In aqueous systems, an A-cation such as Ca(II) forms complexes with oxygen- and fluorine-containing groups, and forms precipitates with such anions as OH^-, F^-, and PO_4^{3-}.

Coulombic influences on cation-ligand affinities must always be present, so that a B-cation such as Cd(II) will evidence a superposition of covalent and electrovalent (coulombic) interactions. Thus, as pointed out by Baes (1973), cadmium (and zinc) are like the IIA metals Ca(II) and Mg(II) in that they form divalent cations of similar ionic sizes. Cadmium forms rather stable complexes with oxygen-atom ligands, and forms rather insoluble precipitates with carbonate. Therefore, Cd(II) forms important complexes with ligands whose donor atoms include S, I, Cl, Br, N, or O. Insoluble precipitates with sulfide, carbonate, and oxalate are also found.

This diversity of ligand preferences on the part of Cd(II), and also Zn(II), has significant implications for the environmental chemistry of cadmium. Since Cd(II) has an ionic radius similar to that of calcium ion [r(Cd) = 0.97 angstroms, r(Ca) = 0.99 angstroms] it may substitute for calcium in solid phases of oxides and carbonate precipitates, and display similar complexing tendencies to Ca(II) where coulombic factors are dominant. As a B-metal cation, with low electronegativity and "soft sphere" characteristics, cadmium forms strong complexes with sulfur-containing ligands (such as cysteine and sulfide), nitrogen-containing ligands (amino acids, ethylenediamine), and oxygen-containing ligands (nitrilotriacetate, citrate, salicylate). Cadmium can thus be expected to compete with a wide range of A-metals, with transition metals, such as Mn(II), Fe(II), Co(II), and with zinc.

It is useful to examine some relative affinity sequences for binding of Cd(II) by various ligands and for the affinity of Cd(II) for a given ligand in comparison to other metals. The basis for such a comparison is the stability constant for complex formation, or, in the case of solid formation, the solubility constant. These constants are functions of temperature, pressure, and the ionic strength (electrolyte content) of the medium. The stability constant for binding of a metal, M, to ligand, L, forming the complex species, ML is

$$\frac{[ML]}{[M][L]} = K$$

Should there be more than one ligand bound per metal ion (stepwise formation), the corresponding cumulative stability constant for complexation is

$$\frac{[ML_n]}{[M][L]^n} = \beta_n$$

For polynuclear complex, M_mL_n, the cumulative stability constant is

$$\frac{[M_mL_n]}{[M]^m[L]^n} = \beta_{mn}$$

For mixed-ligand complexes, involving two (or more) different ligands, P and Q, the cumulative stability constant is

$$\frac{[M_mP_pQ_q]}{[M]^m[P]^p[Q]^q} = \beta_{mpq}$$

For the dissolution of solid MX to give free anion X and free M, the solubility constant is

$$[M][X] = K_{so}$$

The logarithms of the K_{so} values for Cd(II) (Sillen and Martell 1964) solids under dilute solution conditions (15° C) are, approximately

CdS, -29; $Cd(OH)_2$, -14; $CdCO_3$, -13.5

The corresponding K_{so} values for zinc are

ZnS, -23; $Zn(OH)_2$, -17; $ZnCO_3$, -10.5

For divalent mercury only the oxide and the sulfide exist.

HgS, -54; HgO, -25.5

The approximate order of increasing stability of Cd(II) complexes with inorganic ligands, based on pertinent values of log K_f or log β_n/n (Sillen and Martell 1964 and 1971, Gardiner 1974) is: $F^- < Cl^- < Br^- < I^- < SO_4{}^{2-} < NH_3 < PO_4{}^{3-} < OH^- < CO_3{}^{2-} < P_2O_7{}^{4-} < P_3O_{10}{}^{5-} < CN^- < SH^-$. Each of these ligands is known to be present in different environmental situations (seawater, anaerobic reducing sediments, oxygenated surface waters, anaerobic sludges, soil water systems, and so forth). An affinity sequence must be coupled with mass balance constraints for specific systems in order to find the equilibrium distributions of metals, ligands, complexes, and solids. The K_{SO} value does not necessarily indicate that a specific complex or solid will be present under environmental conditions, where competition for ligands and variable oxidation-reduction (redox) conditions may be very important for speciation. That level of complexity is addressed in the discussion of models for environmental systems.

Hg^{2+} is one of the strongest acids found in the earth's crust; it therefore forms complexes with both strong and weak bases (e.g., Se > S > O > N). Mercuric ion reacts very strongly with selenohydryl groups, forming a tighter complex than with sulfhydryl. However, sulfur is much more abundant than selenium in the earth's crust, and so mercury is usually found as either its insoluble sulfide or oxide. Solubilization of inorganic mercury from otherwise insoluble salts such as mercuric sulfide requires oxidation of S^- to $SO_4{}^{2-}$. This oxidation reaction can be catalyzed by microorganisms such as Thiobacilli.

The principal species of mercury found in the sea are $HgCl_4{}^{2-}$ (66 percent), $HgCl_3Br^{2-}$ (12 percent) and $HgCl_3$ (12 percent). The concentration of halogen ions clearly determines this salt composition. In fresh water the ionic composition is less clearly defined because of the low concentration of anions. It is likely that the solubilization of mercury in fresh water systems will be determined by microbial activity in the sediments. For example, the oxidation of S^- to $SO_4{}^{2-}$ by aerobic bacteria, or the release of low molecular weight fatty acids such as acetate, formate, butyrate, propionate, and so on by anaerobic bacteria provide counter ions that will solubilize both mercuric and mercurous ion in fresh water systems.

COORDINATION OF CADMIUM AND MERCURY TO MIXED LIGANDS IN BIOLOGICAL SYSTEMS

As a B-metal cation, Cd(II) shows a strong tendency to bond covalently to sulfur (S) and nitrogen (N) atoms in organic ligands. As remarked above, cadmium also bonds electrovalently to oxygen atoms. Baes (1973) has presented stability constants giving the following affinity sequence for binding of Cd(II) by representative bidentate organic ligands:

ligand:	oxalate <	glycine <	ethylenediamine <	mercaptoethylamine
(atoms):	(OO)	(ON)	(NN)	(NS)

The affinity sequence for various oxygen-donating ligands on the basis of K_1 values is: acetate < oxalate < phthalate < citrate < salicylate < nitrilotriacetate. Cd(II)-amino acid complexes (K_1) (Walker and Williams 1974) appear in the following stability sequence: glycine < phenylalanine < aspartate < histidine < cysteine. Walker and Williams have made equilibrium models of the interactions of Cd(II), Zn(II), Mn(II), Fe(II), and other bivalent metals with amino acids and chelating compounds, such as nitrilotriacetate. They reported that the models show competition between Cd(II) and iron and manganese to be stronger for amino acids than for Cd(II) and Zn(II). Comparison of stability constants for Cd(II)-organic complexes with those for the essential metals (Mn, Fe, Co, Cu, and Zn) and for Hg(II) and Pb(II) led Baes (1973) to the following conclusions:

1. Cd(II) should not displace any of the other essential or toxic metals under consideration from (OO) ligands.

2. Cd(II) should displace Mn(II) and Fe(II) from (NM) ligands, but not Zn(II), Co(II), Ni(II), Cu(II) or Hg(II).

3. Cd(II) is bound more strongly to sulfur than all the metals except Cu(II), Hg(II), and Pb(II) (the latter by a small margin).

Again, it is noted that these are affinity or stability generalizations, and must be examined further in terms of mass balance constraints; however, they are likely to be important predictors in many cases.

The structure of metal-ligand equilibria in aqueous systems embodies: (a) competition between two or more ligands (including OH^- and electrons) for a particular metal ion, (b) competition between two or more metals (including the aqueous proton, H^+) for a given ligand, (c) precipitation and dissolution of solids, (d) adsorption of metals or ligands onto a solid phase (ion-exchange, surface complex formation), and (e) distributions across membranes. The competition among metals for available ligands depends on the stability constants, solubility constants, adsorption constants (or distribution coefficients), and the total concentrations of all metals and ligands in a particular system (Morel and Morgan 1972, Morel et al. 1973).

Comparison of a few stability sequences for complexes of different metals with given ligands is of interest.

Salicylate (OO):

Ca < Cd < Mn(II) < Fe(II) < Zn < Cu(II)

Glycine (ON):

Ca < Mg < Mn(II) < Cd ∿ Fe(II) < Zn ∿ Pb(II) < Cu(II) < Hg(II)

Cysteine (SN):

Mn(II) < Zn < Fe(II) < Cd < Pb(II) < Hg(II)

Hydroxide (O):

Ca < Mg < Cd ∿ Mn(II) < Zn(II) < Co(II) < Fe(II) < Cu(II) < Pb(II) < Hg(II)

Studies of the stabilities of metal binding to ligands should be a very important part of environmental assessments of pollutants. To demonstrate this importance, let us consider the stability sequences for the formation of metal complexes with salicylate. For the metals tested, the calcium complex is the most stable, and the copper complex is the least stable. Thus, calcium easily forms complexes when exposed to salicylate, and if calcium is added to a system in which all available salicylate is completed with other metals, calcium will displace these metals causing them to be re-released to the water column. After all available ligands are bound, all metals added remain undissociated.

These metals will form complexes if more ligands are added. Cadmium, which forms the second most stable complex, can replace all metals except calcium. In this manner, metals can effect the dissociation of other metals. Analysis of a number of metal ions in a particular environmental system allows one to predict the possibility of dissociation into the aqueous phase.

It is clear from these studies that when regulating metals released in wastewater effluents the discharge limitations must consider the potential for mobilizing other metals already present as well as the toxic properties of a metal. Also, assessments of the effects of discharging organic compounds must consider the effect of these compounds on metals already in the receiving streams. Monitoring a single ion in sediment will only be a meaningful exercise if other metal ions with similar properties are also monitored.

The binding of Cd, Cu(II), Zn, and Ni(II) to polygalacturonic acid, $[(\text{-RCOOH})_2]_n$, was studied by Jellinek and Sangal (1972), who found the following increasing stability sequence of complex formation:

$$\mathrm{Ni(II)} < \mathrm{Zn(II)} < \mathrm{CD} < \mathrm{Cu(II)}$$

The relative stability constants for metal binding with elimination of two protons were in the ratios

1 : 1.6 : 218 : 8.2

The adsorption of metal ions onto solid surfaces of silica (SiO_2) and alumina (Al_2O_3) has been interpreted by Schindler (1976) and Hohl and Stumm (1976), respectively, as surface complex formation. On the basis of measured or estimated surface-binding stability constants of Schindler, the order of increasing *affinity* of metals for oxygen on the hydrated SiO_2 surface is

$$\mathrm{Mg} < \mathrm{Ca} < \mathrm{Co(II)} < \mathrm{Cd} < \mathrm{Zn} < \mathrm{Cu(II)} < \mathrm{Pb(II)} < \mathrm{Fe(III)}$$

Cd(II) also forms mixed-ligand complexes in solution. Ternary complexes between Cd(II) and pairs of ligands such as phosphate and tartrate, phosphate and citrate, phosphate and nitrilotriacetate, cysteine and citrate, and cysteine and nitrilotriacetate have been reported by Ramamoorthy and Manning (1975). A quaternary complex, Cd(II)-cysteine-phosphate-nitrilotriacetate, with stability constant $\beta_{mpqr} = 10^{21}$ is reported to predominate at pH values above neutral, for reactant concentrations of 0.003 M. Such systems have not been modeled experimentally or computationally at concentrations typical of those in natural water systems, i.e., micromolar or lower.

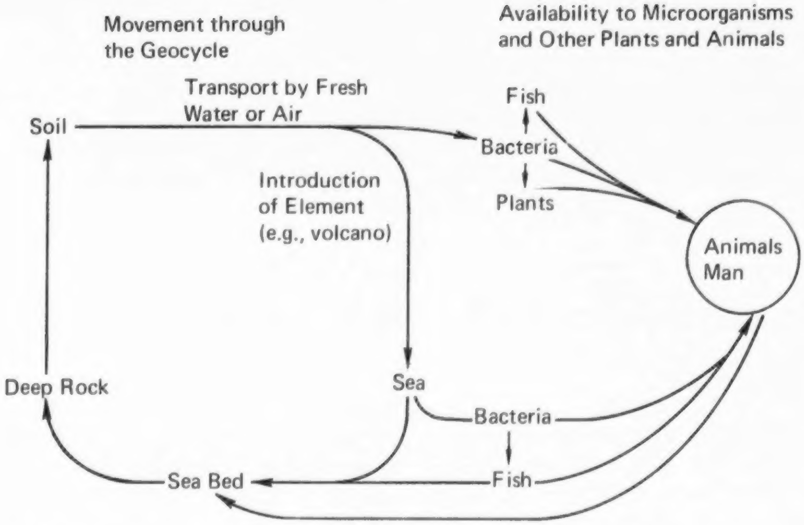
Mercuric ion is such a strong Lewis acid that it binds strongly to both strong and weak anions in the soil. Salt complexes are readily formed between mercuric ion and the so-called fulvic and humic acids. This is not surprising in light of the number of phenolate ions present in these natural products.

Mercury metal is readily adsorbed on particulates in the atmosphere and in water. These systems are so heterogeneous that it is difficult to predict how much metal is transported by such processes.

THE IMPORTANCE OF MICROORGANISMS TO THE MOVEMENT OF TOXIC ELEMENTS

Microorganisms are exceedingly versatile in the way they metabolize natural substances. If microorganisms do not degrade a particular compound, higher organisms are unlikely to be able to do so. Therefore, a study of microbial interconversions of toxic compounds can contribute substantially to environmental science. Because of their potential role in metabolizing toxic substances, microorganisms are vital links in understanding the ways in which such elements move through the environment under natural conditions by way of biogeochemical cycles.

Figure B.2 illustrates the role of microorganisms in getting toxic elements into food chains. The microorganisms involved in this process can be grouped according to their oxygen requirements: (a) aerobes, which degrade compounds oxidatively; (b) anaerobes, which degrade compounds reductively; and (c) facultative anaerobes, which employ both means. Organisms in any of these groups may also hydrolyze, dehydrate, or hydrate compounds. The availability of alternative metabolic pathways facilitates the movement of toxic compounds in the environment. When confronted with a toxic substance, microorganisms frequently adapt to detoxify it. However, the resulting product may be either more or less toxic to higher organisms. To demonstrate the use of this link in the biogeochemical cycle for purposes of identifying


Movement through the Geocycle
Availability to Microorganisms and Other Plants and Animals
Transport by Fresh Water or Air
Soil
Fish
Bacteria
Plants
Introduction of Element (e.g., volcano)
Animals Man
Deep Rock
Sea
Bacteria
Sea Bed
Fish

SOURCE: Wood (1974) Biological Cycles for Elements in the Environment, Wood, J. M., *Science*, Vol. 183, pp. 1049-1052, Fig. 2, 15 March 1974. Copyright 1974 by the American Association for the Advancement of Science.

FIGURE B.2 Movement of Toxic Elements Through the Geocycle

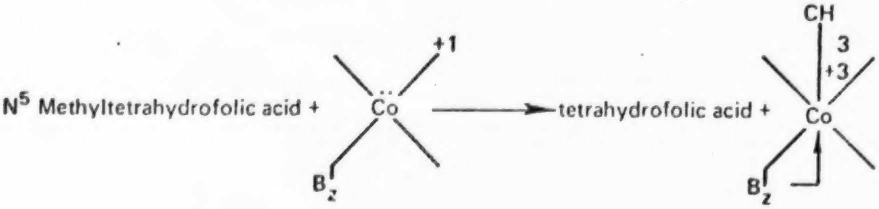
research needs, we shall first trace the movement of the transition metal cobalt, and then examine the relationship between the biochemistry of cobalt and of mercury.

Inorganic cobalt is fixed by certain primitive species of bacteria and incorporated into the vitamin-B_{12} molecule. Vitamin-B_{12} forms the active site of a number of important enzymes, for example, those involved in the biosynthesis of methane gas and of the essential amino acid methionine. In addition, vitamin-B_{12} coenzyme is the active site for a group of enzymes called the "mutases", and for the enzyme ribonucleotide reductase, which catalyzes a crucial step for DNA synthesis in some organisms. After synthesis by microorganisms, vitamin-B_{12} enters food chains and finally is consumed by man. A special protein called the "intrinsic factor" has evolved in higher organisms, which complexes with vitamin-B_{12} (molecular weight of approximately 1400) to form a much larger entity with a molecular weight of approximately 65,000. This complex is transported into the blood stream, where a second group of B_{12}-binding proteins, called the "transcobalamins", remove the B_{12} from intrinsic factor. The transcobalamins are responsible for transport of B_{12} in circulatory systems and function in cellular uptake of the vitamin.

In addition to their role in the transport of cobalt, microorganisms can readily change the oxidation state of the metal, which in turn changes the chemical reactivity of the cobalt atom. For vitamin-B_{12}, the cobalt atom can exist in three alternative oxidation states:

$$\mathrm{Co(III)} + e \longleftrightarrow \mathrm{Co(II)} + e \longleftrightarrow \mathrm{Co(I)}$$

The Co(I) variety of vitamin-B_{12} is very important because it is a good reducing agent and it can be alkylated to produce stable alkyl-B_{12} derivatives. For example, methyl-B_{12} is synthesized in biological systems by the reaction of Co(I)B_{12} and N^5 methyltetrahydrofolic acid:



Methyl-B_{12} holds a key position in the movement of toxic elements in the biosphere because of its involvement in the biomethylation of a number of heavy metals and metalloids. Figure B.3 illustrates how vitamin-B_{12} is involved in the establishment of a biogeochemical cycle for mercury.

In addition to the research conducted on mercury, substantial progress has been made in our understanding of the biomethylation of tin, palladium, gold, arsenic,

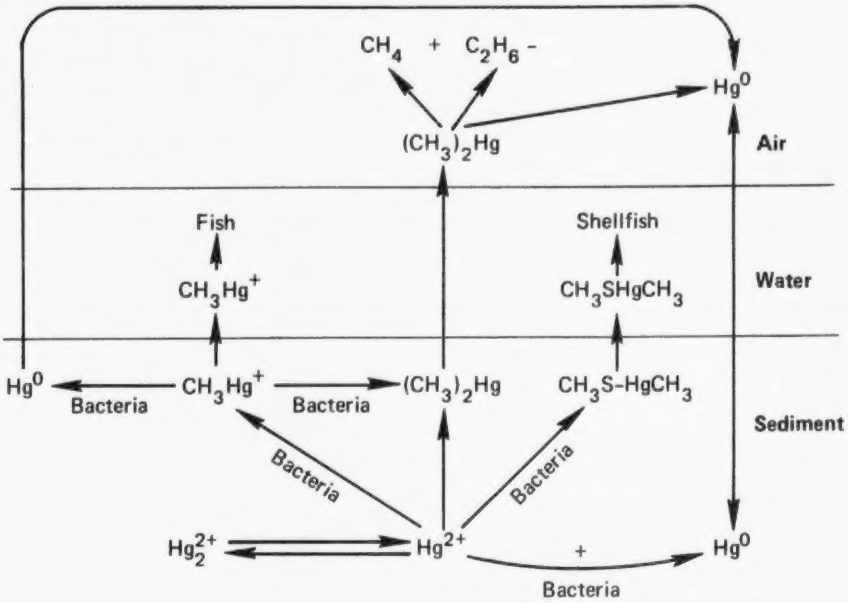

CH_4 + C_2H_6 -
Hg^0
$(CH_3)_2Hg$
Air
Fish
Shellfish
CH_3Hg^+
Water
CH_3SHgCH_3
Hg^0
Bacteria
CH_3Hg^+
Bacteria
$(CH_3)_2Hg$
$CH_3S\text{-}HgCH_3$
Sediment
Bacteria
Bacteria
Hg_2^{2+}
Hg^{2+}
+
Hg^0
Bacteria

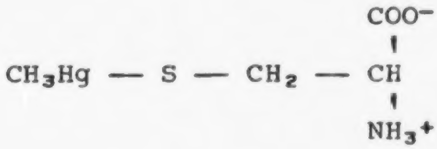
FIGURE B.3 The Mercury Cycle Demonstrating the Bioaccumulation of Mercury in Fish and Shellfish

and selenium. The mechanism of the tin reaction is quite different from that discovered for mercury, even though methyl-B_{12} donates the methyl-group. The stannous ion [Sn(II)] inserts between the cobalt-carbon bond to give a methyl-tin-cobalt structure (CH_3-Sn-Co). The tin-cobalt bond is then broken by a hydroxyl ion (or any other base) to give methyl-stannic ion [CH_3Sn(IV)] and Co(I) B_{12}. Inorganic chemists call such processes oxidative-addition reactions. The significance of the elucidation of mechanisms for biomethylation will be expanded upon later in the section, "The Role of Methyl-B_{12} in the Biosynthesis of Toxic Metal-alkyls."

MEMBRANE TRANSPORT OF METHYLMERCURY AND ITS BIOACCUMULATION

The transport mechanism of molecules such as pesticides, especially chlorinated biphenyls, may clarify the process of bioaccumulation in food chains. Diffusion processes must be important for man-made compounds, since it is unlikely that biological transport mechanisms could have evolved in the time that such synthetic chemicals have been in use. The metalalkyls may also accumulate by the processes of diffusion and partition.

However, methylmercury and other metalalkyls are natural products, so that the possibility of active transport into the cell cannot be ruled out. In humans, methylmercury is secreted into the intestine as the methylmercury-cysteine complex, e.g.:



$$\mathrm{CH_3Hg - S - CH_2 - \underset{\underset{NH_3^+}{|}}{\overset{\overset{COO^-}{|}}{CH}}}$$

The fact that this complex is rapidly transported back into the bloodstream suggests that active transport is involved. In fact, the methylmercury-cysteine complex is probably mistaken for some other amino acid and therefore cannot avoid being transported. Once methylmercury is in the bloodstream, sulfhydryl groups on hemoglobin may distribute it widely throughout the body. This important reaction was studied as early as 1966, when Swedish investigators showed that more than 95 percent of the methylmercury accumulating in fish muscle was present as the methylmercury-cysteine complex (Westoo 1967a,b).

BIOACCUMULATION OF CADMIUM

Concentration factors (the concentration of a substance in an organism divided by the concentration of the substance in aqueous solution) for cadmium of about 900 for marine plankton and brown algae and of about 1600 for freshwater plants have been cited by Bowen (1966), who found concentrations of cadmium in marine and land plants ranging from 0.1 to 4 ppm. Rice and wheat can accumulate significant quantities of cadmium from soil. Soil pH is important to cadmium uptake by plants; more acid soils lead to high concentrations.

Friberg et al. (1974) concluded that itai-itai disease is an expression of chronic cadmium poisoning, resulting from prolonged exposure to high levels of cadmium accumulated in rice grown in polluted areas of Japan. These workers have also shown that cadmium accumulates in various animals, for example, in molluscs and mammalian kidneys. Cadmium proteins have been isolated. The biological half-life of cadmium in man is 10-40 years in the whole body (Friberg et al. 1974). Biological mechanisms for transport and bioaccumulation of cadmium have yet to be elucidated, although there is evidence that cadmium is transported by the normal manganese transport system.

DEMETHYLATION REACTIONS

Enzymes that reduce Hg^{2+} to Hg^0 and CH_3Hg^+ to CH_4 and Hg^0 have been found in a number of enteric bacteria. The reduction of mercuric salts to the metal, which involves a 2-electron transfer from reduced pyridine nucleotide (NADPH), has been reported.

1. Mercuric ion reductase

$$Hg^{2+} + NADPH + H^+ \longrightarrow Hg^0\uparrow + NADP^+ + 2H^+$$

2. Methylmercuric ion reductase

$$CH_3Hg^+ + NADPH + H^+ \longrightarrow CH_4\uparrow + Hg^0\uparrow + NADP^+ \; 2H^+$$

Recent studies in Japan[1] have shown the enzyme that demethylates methylmercury to be a hydrolase, rather than a reductase, e.g.,

$$CH_3Hg^+ + H_2O \longrightarrow CH_4\uparrow + Hg^{2+} + OH^-$$

This hydrolase can be separated from the reductase, which can reduce a number of metal ions (Hg^{2+}, Ag^+, etc.) to their elements. The mechanisms of these nonspecific metal ion reductases may prove commercially very useful for the recovery of noble metals from industrial wastes (e.g., silver from photographic wastes).

THE ROLE OF METHYL-B_{12} IN THE BIOSYNTHESIS OF TOXIC METALALKYLS

Methyl-B_{12} is central in the biosynthesis of environmental metalalkyls. It is involved in the methylation of mercury, tin, palladium, gold, thallium, platinum, selenium, tellurium, sulfur, and arsenic. Most methylated products are much more toxic than their parent elements. Furthermore, some of the products bioaccumulate, and others enter the biosphere because of their volatility. We are just beginning to learn how very significant metabolic cycles for toxic elements are, and about their biogeochemical effects. The most difficult problem to assess is the extent to which man's activities have perturbed natural cycles for toxic elements. The movement of toxic metals in advanced industrial societies not only threatens those societies, but may upset the delicate balance that nature has established for all the elements on this planet.

MODELS FOR SPECIATION OF CADMIUM AND OTHER METALS IN ENVIRONMENTAL SYSTEMS

The influence of a number of different chemical processes must be considered simultaneously in order to predict the speciation, transport, residence times, and fates of trace metals in natural water systems (water, sediments, soils, waste treatment processes). Comprehensive equilibrium models provide an important first approximation to the detailed chemistry of metals and ligands in water under a variety of environmental conditions. Where certain processes in the real system are known to be slow with respect to residence time, kinetic data can be used to develop constrained equilibrium models. Slow steps might include generation of sulfide, decomposition of organic ligands, generation of metallo-organic compounds, oxidative dissolution of metal ion precipitates, transfer of metals by flocculation and sedimentation, and so on. For the processes that can be well-approximated by an equilibrium description, the important inputs to a multimetal, multiligand model are as follows: temperature, pertinent equilibrium constants for complex formation (association and dissociation), solubility constants for sparingly-soluble precipitates, total concentrations of all metals and ligands, nature and area of adsorbing surfaces, equilibrium constants for adsorption, and oxidation-reduction thermodynamic data. Acid-base and oxidation-reduction states of the system can be described in terms of pH and pE (or redox potential), respectively. These variables are of a logarithmic nature, ranging from 4 to 10 for pH (6 orders of magnitude) and from -5 to 12 for pE (17 orders of magnitude).

General Predictions

As a result of studies based on the foregoing description of complex formation and solubility properties of Cd(II), important qualitative predictions about the aqueous environmental behavior of cadmium are suggested. The great affinity for sulfur in reduced form (sulfide, cysteine) predicts a low concentration of free aqueous cadmium in strongly anaerobic environments, in which sulfate is reduced to sulfide. Thus, although there is no redox chemistry for cadmium itself under aqueous conditions, redox equilibria and rate processes will play a major role in cadmium regulation. Under mildly reducing conditions, precipitation of $CdCO_3$ is a distinct possibility, and will be strongly influenced by the alkalinity of the water and the pH of the system. In marine environments, halides can be expected to play a major role in determining speciation. Carbonate may also contribute to cadmium complexation. The solubility constants for $CdCO_3$ and $Cd(OH)_2$ indicate that the carbonate will be the stable solid (in the absence of high sulfide concentrations) for normal atmospheric partial pressures of carbon dioxide. If cadmium enters natural waters as oxide particles, solubilization and possible conversion to the carbonate should be expected. Particulate fractions of cadmium in natural waters are likely to exist in several forms, depending upon their source: slowly reactive oxide solids; $CdCO_3$ solid, or solid solution of $CdCO_3$ in $CaCO_3$ precipitates; cadmium adsorbed on aluminum, iron, silicon, or manganese oxide phases; cadmium held in exchange positions on clays; cadmium bound to organic particles (humic material, plant debris) by oxygen or nitrogen groups; and slowly-dissolving CdS solid particles introduced by discharge of strongly anoxic, sulfur-rich effluents or sludges, or dredged up to aerobic environments from anaerobic deposits.

Equilibrium Computer Models for Cd(II) Speciation in Natural Waters

Insights into the chemical behavior of cadmium in natural water systems have been gained by constructing multimetal, multiligand models in which the influences of pH, pE, adsorption, and total system concentrations of all pertinent metals and ligands are examined at levels characteristic of different natural waters. The abiotic distribution of cadmium in aquatic environments may be visualized according to the simple scheme shown in Figure B.4.

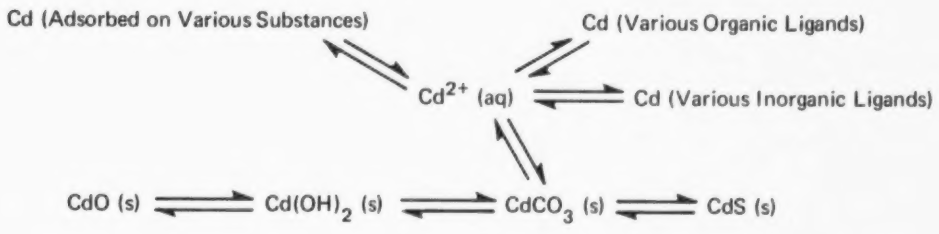

Cd (Adsorbed on Various Substances)
Cd (Various Organic Ligands)
Cd2+ (aq)
Cd (Various Inorganic Ligands)
CdO (s)
Cd(OH)2 (s)
CdCO3 (s)
CdS (s)

FIGURE B.4 Scheme for Abiotic Distribution of Cadmium in Aquatic Systems

In principle, every metal and every ligand in a system may interact with cadmium (or any other metal) directly or indirectly. In fact, a few interactions are usually dominant (Morel et al. 1973). Carbonate ions, protons, and organic ligands tend to be agents for mediating interactions among metals for scarce ligands, and among ligands for metals and protons. In the case of cadmium, organic ligands tend to solubilize the adsorbed form or the carbonate (oxidized or reduced environment) and the sulfide (reduced environments). Chloride (and perhaps mixed halogenide) complexes should be dominant influences for solubilizing, or desorbing in marine waters. In general, freshwater models have shown the greatest interaction (i.e., free Cd^{2+} concentration dependent upon variations of another metal or ligand) in systems containing a mixture of several organic ligands, carbonate, calcium, magnesium, and trace metals, particularly Cu, Zn, and Pb (Morel et al. 1973).

Freshwater equilibrium models (low chloride, sulfate; low ionic strength; variable particulate content for adsorption) reveal typical patterns when all major metals and ligands and a representative set of trace metals and minor organic and inorganic ligands are included (Ca, Mg, Na, K, Sr, Fe, Mn, Cu, Zn, Ni, Hg, Pb, Co, Ag, Cr; CO_3, SO_4, Cl, NO_3, F, Br, NH_3, PO_4, in addition to Cd). $CdCO_3$ precipitates in many cases, and thus adsorption onto such surfaces as silica, iron oxide, and manganese dioxide is minimized. If citrate is present as a ligand, one-third of the cadmium may be in complex form, and precipitation of $CdCO_3$ is prevented. Wide variations in organically complexed cadmium are brought about by alterations in pH between 6 and 8. Among the adsorbents silica, iron oxide, and manganese dioxide, the last yields the strongest adsorption per unit area of adsorbent at neutral pH. Among the organic ligands considered (cysteine excluded), citrate and nitrilotriacetate bind cadmium most extensively in the presence of oxygen, even though these ligands are themselves bound up with Ca, Cu(II), Fe(III), Ni(II), Mg, and Pb(II). There is pH-dependent competition between carbonate and citrate in complexing Cd over the pH range 6 to 9. Mixing models for typical fresh waters and seawaters show dissolution of $CdCO_3$ present in the fresh water system, and conversion of essentially all cadmium to the $CdCl_2$ complex, in agreement with the observations of Stumm and Brauner (1975) on trace metals in seawater. Details of the freshwater models for cadmium can be found in Morel et al. (1973), Sibley and Morgan (1976), and Vuceta (1976).

The overall impression from oxygenated freshwater models is that the major forms of Cd will be: Cd^{2+}, $CdCO_3$ (solid), $CdCO_3$ (complex), soluble complexes of cadmium with carboxylic acids, and cadmium adsorbed to Mn oxides. Exchange on clays has not been considered, but is certainly likely. Adsorption to organic particulate matter with carboxylic groups is expected, but descriptive data are not available on this mechanism. $CdCO_3$ regulates soluble Cd(II), and solid solutions of $CdCO_3$ in calcium carbonate solid would set lower concentration limits than would a pure $CdCO_3$ solid.

Cadmium binding by humic substances in solution requires further experimental work. Model studies with salicylate as a ligand show very little binding of Cd(II) at total cadmium concentrations around 1 μg/l and pH ranges from 6 to 8. Under such conditions, given the stability constants for Cd(II)-salicylate complexation, protonation of salicylate, and complexation of salicylate by other cations, less than 0.1 percent of cadmium is bound to this organic ligand. At pH 8, the only metal predicted to be bound to an appreciable extent (about 20 percent) is Cu(II). Marine models show weak binding of cadmium by phthalate, a benzene dicarboxylic acid, and stronger (but still quantitatively unimportant) binding by acetate, citrate, and tartrate (Stumm and Brauner 1975). Chloride complexes are predominant in marine waters under oxidized conditions.

Sewage Speciation Models

CdS(s) and $CdCO_3$(s) are predicted to occur under reducing conditions and relatively high cadmium concentrations in primary effluents and sewage sludges (10-100 μg/l; up to 200 mg/kg in solid fractions). When the pE is below about -3 (-0.2 volts redox potential), the sulfide phase forms; the carbonate phase appears under conditions of greater oxidation (Morel et al. 1975). Solution-phase cadmium is depressed to extremely low levels under conditions of CdS(s) formation, the soluble species being Cd(II)- sulfide complexes. Similar findings have been reported by Leckie and Nelson (1975) for anaerobic sediments under marine conditions: a transition from $CdCO_3$(s) to CdS(s) is predicted at pE -3.5. In the presence of $CdCO_3$, chloro complexes are the predominant solution form (amounting to about 6 μg/l). Complexation by cysteine, histidine, and polycarboxylic acids can be predicted to enhance cadmium solubility in sediments and sludges where no oxygen is present, although data are still inadequate to make model computations (Morgan and Sibley 1975). Under highly reductive conditions, adsorption onto mineral surfaces (quartz, aluminum oxides) cannot compete with sulfide precipitation as a control over Cd(II) in solution. As sediments, sludges, or effluents become oxidized, adsorbing surfaces must compete with chloride in marine waters or with carbonate and organic ligands in fresh waters to regulate free cadmium levels in the solutions. Mobilization as chloro or organic complexes is highly dependent upon the redox chemistry of the sediment, sludge, or soil-water system. This area is clearly one in which kinetic considerations (e.g., rates of dissolution of solid phases, oxidation of sulfur-containing ligands) constrain the applicability of equilibrium models. If CdS(s) particles in sewage are diluted with seawater without oxidation of the reduced sulfur, a dilution of greater than 10^4 is required to dissolve the solid and form the chloro complex, $CdCl_2$(aq). $CdCO_3$(s) is not formed upon dilution of sewage with seawater.

IDENTIFICATION OF RESEARCH NEEDS FROM MERCURY EXAMPLE

The data in Table B.1 demonstrate that a great deal of information can be extrapolated from an understanding of the metabolic routes for mercury in the environment. For example, we can predict that the environmental biomethylation of Sn, As, Se, Te, Pd, Pt, Au, Tl, and Pb would produce metalalkyls or metalloidalkyls capable of bioaccumulation because of their lipid solubility. Research is needed on the delineation of metabolic routes and the examination of the kinetics for the uptake of metalalkyls by both diffusion-controlled and active transport mechanisms. Partitioning of metalalkyls into phospholipids, especially into cell membranes of the central nervous system, is now especially pertinent. Recent publications on the biomethylation of lead are of special significance because alkyl-lead compounds are neurotoxins, and advanced industrial society has converted large quantities of insoluble lead complexes into soluble and available lead salts which have been released to the air and water.

Fates of metalalkyls must be studied in at least two major research areas, which apply to methylmercury as well as to other biomethylated elements that are less well understood:

- Field studies on the movement of metalalkyls in food chains should be made, and active transport and diffusion-controlled processes identified.

- Kinetic studies on membrane uptake and transport and lipoprotein partition of metalalkyls in biological systems would lead to a clarification of the rate and potential of metalalkyl accumulation.

EXTRAPOLATION OF THE MERCURY EXAMPLE TO OTHER TOXIC ELEMENTS

Other metals capable of existing as stable metalalkyl compounds in aqueous systems should be carefully studied, but the assumption that they will strictly fit the mercury model is tentative. For example, methyl-B_{12} has been shown to react with Hg^{2+}, Sn^{2+}, and Pb^{2+} but the mechanisms involved appear to be quite different (i.e., electrophilic attack, oxidative addition, and nucleophilic attack). It is likely that Hg^{2+} will be methylated primarily in an aerobic environment, but tin and lead can only be appreciably methylated in anaerobic or facultative anaerobic situations. An understanding of detailed reaction mechanisms can give valuable clues as to what sector of the environment should be observed.

Cadmium does not form stable metalalkyls, and therefore is more likely to bioaccumulate as a coordination complex (e.g., by natural Zn^{2+} or Mn^{2+} transport systems). Cadmium and zinc share similar modes of environmental transport and bioaccumulation, but the only features common to Hg^{2+} and Cd^{2+} are their divalent nature and characteristic coordination to sulfur donors.

The periodic table can be used to predict some of the properties of heavy metals, and hence the behavior of these compounds in geochemical cycles. However, the involvement of biological processes considerably complicates this exercise.

RESEARCH NEEDED ON CADMIUM IN THE ENVIRONMENT

Figure B.5 illustrates some of the basic environmental flows and fates of cadmium as well as of other trace metals. One of the primary obstacles to predicting the flow of cadmium in specific urban environments is the lack of detailed emission inventories. Major sources and their strengths must be identified, as should cadmium concentrations in different size classes. Such information has significant implications for predicting the impact of atmospheric sources on land and aquatic reservoirs. Some suggestions for areas of research are outlined in the following discussion.

- Study directed toward precipitation and dissolution rates of sulfide phases of cadmium and other metals forming solid solutions with cadmium will aid in predicting cadmium mobilization from sludges, sediments, and soil particles.

- Interactions of naturally-occurring and man-made chelating agents with cadmium must be studied in order to identify mobilization mechanisms and rates in sediments and soils. Sulfur-containing chelating agents and polycarboxylic acids (nitrilotriacetate, for example) should be examined from the point of view of solubilization and desorption of cadmium in particles. These processes promote the release of cadmium to overlying waters or increase availability to plants. The existence of naturally-occurring or pollutant ligands with unusually high affinities for Cd(II) should be investigated.

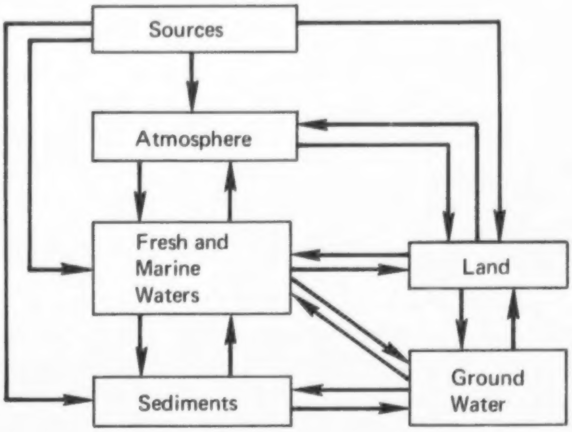


FIGURE B.5 General Environmental Flow Chart for Trace Metals

- Field-level studies are needed in order to elucidate cadmium turnover in natural systems. It is particularly important to better understand rates of cadmium accumulation by phytoplankton and zooplankton under the physical and chemical conditions encountered in surface waters of marine, fresh water, and estuarine systems.

- The solution chemistry of Cd(II) with respect to formation of carbonate complexes needs definition. Reports of cadmium carbonate complexes have been received skeptically by some researchers. The existence of such species affects adsorption of cadmium onto surfaces, and hence its residence time in surface waters.

- Too little attention has been given to sediment reservoirs of metal pollutants. At any given time, only a small part of the total cadmium in an aquatic system is in the body of the water. Suspended and sedimented particles need to be more completely characterized with respect to metals content, particle sizes, redox environment, flocculation and sedimentation rates, etc. Especially important is the characterization of the acid-base chemistry and metal-binding tendencies of the functional groups on mineral and organic surfaces.

NOTE

1 Kenzo Tonomura, Fermentation Research Institute, Agency of Industrial Science and Technology, Ministry of International Trade and Industry, Inage Schiba City, Japan, personal communication, 1976, to Karen Beijer, Swedish Air and Water Quality Laboratory.

REFERENCES

Baes, C.F., Jr. (1973) The properties of cadmium. Pages 29-46, Cadmium: The Dissipated Element, edited by W. Fulkerson and H.E. Goeller. Oak Ridge, Tenn.: Oak Ridge National Laboratory.

Bowen, H.J.M. (1966) Trace Elements in Biochemistry. New York: Academic Press.

Friberg, L., M. Piscator, G.F. Nordberg, and T. Kjellstrom (1974) Cadmium in the Environment. 2nd ed. Cleveland, Ohio: Chemical Rubber Press.

Gardiner, J. (1974) The chemistry of cadmium in natural water - I. A study of Cd complex formation using the cadmium specific ion electrode. Water Research 8:23-30.

Garrels, R.M., F.T. Mackenzie, and C. Hunt (1975) Chemical Cycles and the Global Environment. Los Altos, Calif.: William Kaufmann.

Hohl, H. and W. Stumm (1976) Interaction of lead (2+) with hydrous α-alumina. Journal of Colloid and Interface Science 55(2):281-288.

Jellinek, H.H.G. and S.P. Sangal (1972) Complexation of metal ions with natural polyelectrolytes. Water Research 6:305-314.

Jernelov, A. (1974) Heavy metals, metalloids, and synthetic organics. Pages 799-815, Sea, edited by M.N. Hill, A.E. Maxwell, and E.D. Goldberg. New York: John Wiley.

Leckie, J.O. and M.B. Nelson (1975) Role of Natural Heterogeneous Sulfide Systems in Controlling the Concentration and Distribution of Heavy Metals. Presented at the Second International Symposium on Environmental Biogeochemistry, April 1975, Burlington, Ontario. Preprints available from J.O. Leckie, Department of Civil Engineering, Stanford University, Calif.

Morel, F.M. and J.J. Morgan (1972) A numerical method for computing equilibria in aqueous chemical systems. Environmental Science and Technology 6(1):58-71.

Morel, F., R.E. McDuff, and J.J. Morgan (1973) Interactions and chemostasis in aquatic chemical systems: Role of pH, pE, solubility, and complexation. Pages 157-200, Trace Metals and Metal-Organic Interactions in Natural Waters, edited by P.C. Singer. Ann Arbor, Mich.: Ann Arbor Science Publishers.

Morel, F.M.M., J.C. Westall, C.R. O'Melia, and J.J. Morgan (1975) Fate of trace metals in Los Angeles County wastewater discharge. Environmental Science Technology 9(8):756-761.

Morgan, J.J. and T.H. Sibley (1975) Chemical models for metals in coastal environments. Pages 1332-1352, Civil Engineering in the Oceans, No. 3. Proceedings, American Society of Civil Engineers. Specialty of Delaware, Newark, Delaware, June 9-12, 1975. New York: American Society of Civil Engineers.

Ramamoorthy, S. and P.G. Manning (1975) Equilibrium studies of solutions containing Al^{3+}, Cab$_2^+$, or Cdb$_2^+$ and cysteine, orthophosphate and a carboxylic acid. Journal of Inorganic Nuclear Chemistry. 37:363-367.

Schindler, P.W. (1976) The regulation of trace metal concentrations in natural water systems: A chemical approach. Proceedings of the First Special Symposium on Atmospheric Contributions to the Chemistry of Lake Waters, September 28-October 1, 1975, Geneva Park, Ontario. Sponsored by the International Association for Great Lakes Research. Journal for Great Lakes Research 2(Supplement 1):132-145.

Sibley, T.H. and J.J. Morgan (1976) Equilibrium Speciation of Trace Metals in Freshwater: Seawater Mixtures. Pasadena: Keck Laboratories, California Institute of Technology.

Sillen, L.G. and A.E. Martell (1964) Stability Constants of Metal-Ion Complexes. London: The Chemical Society.

Sillen, L.G. and A.E. Martell (1971) Stability Constants of Metal-Ion Complexes. Supplement No. 1. London: The Chemical Society.

Stumm, W. and P.A. Brauner (1975) Chemical speciation. Pages 173-239, Chemical Oceanography, edited by J.P. Riley and G. Skirrow. 2nd ed. Volume 1. New York: Academic Press.

Vuceta, J. (1976) Adsorption of Pb (II) and Cu(II) on α-Quartz from Aqueous Solution. Thesis. Pasadena: California Institute of Technology.

Walker, M.D. and D.R. Williams (1974) Thermodynamic considerations in coordination Part XVIII: Formation constants for cadmium (II)--Amino acid complexes as determined by glass and solid-state cadmium-electrode potentiometry. Journal of the Chemical Society, Dalton, Transactions (London) 1974 (11):1186-1189.

Westoo, G. (1967a) Methylmercury in fish. Acta Chemica Scandanavica 21:1790-1797.

Westoo, G. (1967b) Methylmercury in food. Var Foeda 19:121-127.

Wood, J.M. (1974) Biological cycles for elements in the environment. Science 183:1049-1054.

Wood, J.M. (1975) Biological cycles for elements in the environment. Die Naturwissenschaften 8:357-365.

BIBLIOGRAPHY

Crerar, D.A. and H.L. Barnes (1974) Deposition of deep-sea manganese nodules. Geochimica et Cosmochimica Acta 38(2): 279-300.

Dagley, S. (1975) A Biochemical Approach to Some Problems of Environmental Pollution. Pages 81-138, Essays in Biochemistry, Vol. 11, Edited by P.N. Campbell and F. Dickens. Published for the Biochemical Society (of England). Boston: Academic Press.

Eaton, A.D. (1974) Marine Geochemistry of Cadmium, Thesis. Cambridge, Mass.: Harvard University.

Gardiner, J. (1974) The chemistry of cadmium in natural water - II. The adsorption of cadmium on river muds and naturally-occurring solids. Water Research 8:157-164.

Guy, R.D., C. L. Chakrabarti, and L.L. Schramm (1975) The application of a simple chemical model of natural waters to metal fixation in particulate matter. Canadian Journal of Chemistry 53(5):661-669.

Jarvie, A.W.P., R.N. Markall, and H.R. Potter (1975) Chemical alkylation of lead. Nature 255(5505):217-218.

Jenne, E.A. (1972) Mercury in Waters of the United States. Menlo Park, Calif.: U.S. Geological Survey.

Kubota, J., E. L. Mills, and R.I. Oglesby (1974) Lead, Cd, Zn, Cu, and Co in streams and lake waters of Cayuga Lake Basin, New York. Environmental Science Technology 8:243-248.

Lien, E.L., L. Ellenbogen, P.Y. Law, and J.M. Wood. (1974) Studies on the mechanism of cobalamin-binding to Hog intrinsic factor. Journal of Biological Chemistry 249(3):890-894.

Rohatgi, N. and K.Y. Chen (1975) Transport of trace metals by suspended particulates upon mixing with seawater. Journal of the Water Pollution Control Federation 47:2298-2316.

Schmidt, U. and F. Huber (1975) Methylation of organolead and lead (II) compounds to $(CH_3)_4Pb$ by microorganisms. Nature 259(5539):157-158.

Wong, P.T.S., Y.K. Chan, and P.L. Luxon (1975) Methylation of lead in the environment. Nature 253:263-264.

Wood, J.M. (1971) Environmental pollution by mercury. Pages 39-56, Advances in Environmental Science and Technology, Volume II, edited by J.N. Pitts and R.L. Metcalf. New York: Interscience Publications.

Wood, J.M. (1972) Interconversions of poisonous elements in the environment. American Paint Journal 57(13):87-95.

Wood, J.M. (1973) Toxic elements in the environment. Revue Internationale d'Oceanographie Medicale, (M. Aubert, ed.) T31/32:7-16.

Wood, J.M. (1974) Metabolic cycles for toxic elements in the environment. Pages 105-112, A Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes, edited by R.G. Wilkins. New York: Allyn and Bacon.

Wood, J.M. (1975) Mechanisms for the biosynthesis and neurotoxicity of methylmercury. Pages 377-389, Organotransition-Metal Chemistry, edited by Y. Ishii and M. Tsutsui. Proceedings of the First Japanese-American Seminar on Prospects in Organotransition-Metal Chemistry, University of Hawaii's East-West Center, Honolulu, May 1-3, 1974. New York: Plenum Press.

Wood, J.M. and Brown, D.G. (1972) The chemistry of vitamin B_{12}-enzymes. Pages 47-105, Structure and Bonding. New York: Springer Verlag.

Wood, J.M., F.S. Kennedy, and C.G. Rosen (1968) The synthesis of methylmercury compounds by methanogenic bacteria. Nature 220:173-175.

Wood, J.M., M.W. Penley, and R.E. DeSimone (1972) Mechanisms for methylation of mercury in the environment. Pages 49-65, Mercury Contamination in Man and his Environment. Vienna: International Atomic Energy Agency.

APPENDIX C

ORGANIC CHEMICALS:

EXAMPLES OF SYNTHETIC MATERIALS

Public concern about the presence of synthetic chemicals in the environment arises from three properties that vary greatly in importance from one type of compound to another: toxicity, persistence, and accumulation in food chains. Of these, persistence and accumulation--which deal with resistance to degradation and the potential for storage in fatty tissues--may be determined through the study of the environmental transport and transformation of synthetic organic chemicals. Also important are the potential for wide distribution throughout the environment, the distribution of a material among the various components of the environment, and the rates at which both transport and transformations occur.

These factors are interrelated. A nonpersistent compound will have limited potential for distribution throughout the environment and for accumulation. The rates at which transformations occur influence the degree of persistence. All of these characteristics are therefore important determinants of the fate of a synthetic organic compound.

These characteristics are largely determined by the physical and chemical properties of the molecules involved and by the degree of similarity to naturally-occurring substances. For example, solubility properties are important for chemicals that are not incorporated into a cell by active transport mechanisms, since these chemicals will be able to penetrate a cell to the extent that they are capable of diffusing through the lipid portions of the cell membrane.

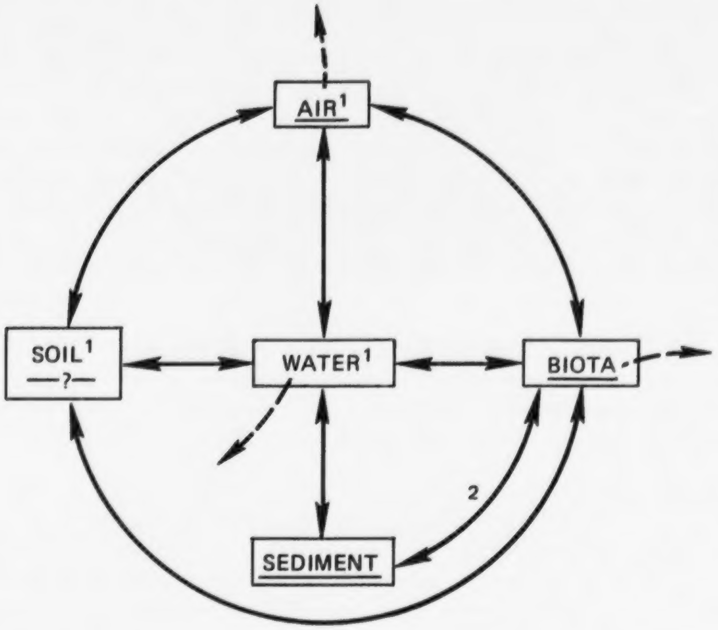
Figure C.1 depicts a general cycle for environmental transport and transformation of persistent organic compounds. The solid lines show the pathways for movement among the various components of the cycle. The underlined words represent common sinks, or sites for accumulation. The dashed lines indicate the transformation processes, which result in the conversion of persistent synthetic organic compounds to substances such as CO_2, and which then enter carbon, oxygen, and other cycles.

The environmental cycle for synthetic organic compounds shows important similarities and differences when compared with previously-described cycles. Organic compounds, like others, move through all parts of the environment and they can be degraded, although the process may occur very slowly.

An important difference is the tendency for persistent organic compounds to accumulate in certain places in the environment where they may remain essentially unchanged for extended periods of time. The sites for accumulation are often within organisms (e.g., adipose tissues) or in materials closely associated with them (e.g., sediments). In such locations accumulation to toxic levels may occur, and the potential for sudden release from these sites exists. Accumulation within living organisms also tends to minimize metabolic degradation due to partitioning into adipose tissues. Since synthetic organic compounds are transferred from one organism to another through predation, the potential for accumulation to toxic levels increases at higher trophic levels (Metcalf et al. 1972). The organisms most affected may be far removed from the initial site of environmental exposure. Indeed, the bioaccumulation process may serve as a means for transport of persistent compounds. Migratory birds, for instance, have been shown to transport pesticides to the tundra areas (Persson 1972, Anderson and Hickey 1976; Enderson and Berger 1968).

A second important difference of the environmental cycle for synthetic organic compounds is that the cycle does not involve degradation of the compounds to simple molecules followed by eventual resynthesis of the original compound. Since the degradation products are incorporated into the biogeochemical cycles for other materials, the environmental cycle for synthetic compounds simply traces their movement throughout the environment until they are incorporated into other, natural cycles.

Mechanisms do exist for the degradation of persistent organic compounds, for their elimination from organisms, and for detoxification. Bacteria are the primary organisms for degradation. In higher organisms, although some catabolic pathways have been shown to develop for synthetic chemicals, the result has sometimes been an increase rather than a decrease in toxicity (Metcalf et al. 1972). Once these compounds are incorporated into an organism, the primary mechanism for their elimination seems to rely on diffusion. Since the kinetics of the process generally favor concentration in lipids rather than water, the rate of elimination is often very slow.


AIR[1]
SOIL[1]
—?—
WATER[1]
BIOTA
SEDIMENT
2

[1] Anthropogenic discharges
[2] The rate of uptake by the biota depends largely on extent of physical transport of sediments and upon whether anaerobic or aerobic conditions exist.

FIGURE C.1 Environmental Cycle of Persistent Synthetic Chemicals

A fundamental problem with the degradation of such materials seems to be that the compounds are not retained in components of the environment that are conducive to degradation long enough to be significantly reduced. Higher molecular weight polychlorinated biphenyls (PCBs) present an excellent example. When discharged in aqueous effluents, PCBs vaporize to the atmosphere, are taken up by aquatic organisms, or are adsorbed to particulates that eventually settle out as part of the sediment. In the biota, the preference of PCBs for fatty tissue minimizes degradation within macroorganisms. Organisms capable of degrading PCBs exist primarily in habitats where these materials are not the preferential substrate. In sediments, PCBs have been shown to persist for several years, and evidence favors stability in the atmosphere. Furthermore, PCBs are quickly adsorbed onto particulates. The photolytic mechanism for degradation has a limited effect, possibly because the intricate crevices of these particles afford them a measure of protection from light. The PCBs are distributed by wind action upon the particles and are reintroduced to water in rainfall.

The general concepts depicted in Figure C.1 also reveal important gaps in knowledge. For most compounds, the rates for transfer among the parts of the cycle are not known. It is important that this information be researched.

Another area of uncertainty involves the extent to which the soil is a site of accumulation of persistent organics. In arid climates, organic compounds that seep into soils may remain adsorbed to soil particles for many years. Important processes for removal would be sublimation and surface erosion. In areas that receive more rainfall, removal is possible at much faster rates, since organic compounds added to soils are subjected to wind and rain erosion, sublimation, leaching to water tables, uptake by plants and animals, and degradation by soil organisms. However, the compounds may also accumulate by adsorption to clay particles or to humic material. Thus competing processes of adsorption and removal exist in soils. Site-specific studies are needed to determine which process will predominate in a given location.

Although, as is shown in Figure C.1, the atmosphere acts as a reservoir for organics, this capacity depends to a great extent on the compound involved. Chlorinated hydrocarbons of low molecular weight evaporate rapidly and may be present in insignificant amounts in other media. The degree to which photolytic processes are important to degradation remains to be quantified. However, free radical reactions have been shown to be important mechanisms for degradation of such hydrocarbons in the atmosphere. Adsorption of these molecules to particulates may also protect them from photooxidation and thus serve as a means for their reintroduction to land and water.

Compounds with higher molecular weights may vaporize from water surfaces (Acree et al. 1963) and from plants and soils (Nash and Beall 1970). Particulate adsorption is probably an important means for reintroducing such substances to soil and to water (Tarrant and Tatton 1968, Yates et al. 1970). Volatile organic compounds undergo numerous changes upon exposure to ultraviolet radiation, and, as Crosby (1972) has suggested, the atmosphere may act as a huge photochemical furnace that can "burn" compounds to nontoxic products. For example, it appears that photochemical destruction of particulate adsorbed polycyclic aromatic hydrocarbons (PAHs) plays a large role in the conversion of PAHs to more oxidized forms. The degree to which the process of photochemical oxidation contributes to the overall disappearance of organic compounds has not, however, been assessed, and the degree to which organic compounds persist in the atmosphere despite the process has not been demonstrated. What is more certain is that radiation may modify chemical structures. Pyrethrins (Chen and Casida 1969) and rotenone (Jones and Haller 1931, Cahn et al. 1945) have been shown to undergo rapid photooxidation. Aldrin is readily oxidized to the more toxic dieldrin (Rosen and Sutherland 1967), and parathion is converted into the extremely poisonous paraoxon, although subsequent reactions in the presence of light reduce the overall toxicity (Frawley et al. 1958).

Finally, it is important to emphasize that the key to understanding the fate of any synthetic substances (and to categorizing and evaluating the many synthetic compounds manufactured) is the consideration of their physical and chemical properties and the way these properties determine the response of the compound to the biogeochemical forces that act upon all things.

It may be convincingly argued, particularly with an increasing world population, that humanity needs the continued use of insecticides to control diseases such as malaria and sleeping sickness, and of other chemicals to protect crops. Moreover, the current worldwide increase in chemical technology entails increasing risks of accidental release of man-made compounds into the biosphere. It is therefore evident that we need to understand those processes that are responsible for removing organic chemicals from the environment. Of these, biodegradation by microorganisms is the most important, and will be discussed in some detail.

BIODEGRADATION OF SYNTHETIC COMPOUNDS

A man-made compound will be biodegradable if it is susceptible to attack by the enzymic apparatus acquired by microbes during evolution. This susceptibility depends first upon the ability of microbial enzymes to accept as substrates compounds having chemical structures similar to, but not identical with, those found in nature; and second upon the ability of these novel substrates, when in the presence of microbes, to induce or derepress the synthesis of the necessary degradative enzymes.

Biodegradability is less likely to be achieved when structural features that are never encountered in natural products are incorporated into a molecule. Conversely, when the para chlorine atoms of DDT are replaced by methoxyl groups--very common substituents of the benzene nucleus in natural products--the resulting pesticide, methoxychlor, is much more readily metabolized by microbes than was the original DDT. The study of biodegradability, therefore, is linked inevitably with the study of both the mechanisms of induction and the modes of action of those enzymes employed for degrading natural products. In any laboratory study of man-made molecules, there will come a point at which experimental findings must be interpreted within the framework of knowledge of microbial catabolism in general.

The degradative reactions catalyzed by microorganisms serve an indispensable function in the carbon cycle. The biosphere contains vast quantities of biochemically inert material that is not metabolized by other living forms. Some of this material, such as the complex three-dimensional polymer lignin, has played a part--as structural material--in plant evolution. Other smaller structures, such as numerous alkaloids and terpenes, have less obvious physiological significance, but this does not alter the fact that they are synthesized in great abundance, and when they have served whatever purpose they have, they must be degraded if the carbon cycle is to function continuously, so that CO_2 may be released and replenished for photosynthesis. The main agents of this process are aerobic microorganisms, which display a remarkable versatility in degrading organic compounds to carbon dioxide and water, using the energy released and the biochemicals formed to serve the requirements of growth. Investigations during the last two decades have provided some of the reasons for this unique degradative ability. Aerobic microbes make use of most of the biochemical sequences and cycles that occupy a central position in metabolic charts and are generally found in other living forms. But, in addition, they possess the unique biochemical asset of being able to catalyze the oxidation of numerous natural products using molecular oxygen. In this way they initiate reaction sequences that enter the central pathways of metabolism--such as the Krebs cycle or the fatty acid "spiral". Thus, an alkane remains biochemically inert until a terminal carbon has been oxidized. The fatty acid so formed may then enter a main channel of metabolism, namely, β-oxidation. The unsubstituted benzene nucleus is an inert resonance structure, but the substitution of two hydroxyl groups placed either ortho or para to each other allows enzymic ring-fission to take place. The benzene ring occurs in the second most abundant polymer in nature (lignin) and in a great number of natural products of lower molecular weights. It is also a structural feature of many pesticides and of many industrial products, notably those of the petroleum and coal-based industries. The benzene nucleus can be cleaved anaerobically and it is probable that anaerobic organisms make a significant contribution to carbon turnover in general. In the future, anaerobes may well become increasingly responsible for degrading benzenoid compounds anaerobically with nitrate as electron acceptor (Taylor et al. 1970), now that accumulation of nitrate supplied by synthetic fertilizers is sufficient to cause concern in some localities (National Research Council [NRC] 1974a). Evidence exists that anaerobic reactions initiate the degradation of certain pesticides. However, there is also little doubt that the complete conversion of a vast range of organic compounds to CO_2 and water in our environment depends upon the ability of microorganisms to initiate attack upon inert biochemical structures by activating molecular oxygen. A few general observations about this process will therefore be made since, as Dagley (1975b) has indicated, a new perspective--one that complements traditional biochemical viewpoints--is called for.

Most biochemical studies have been made upon individual organisms and their enzymes. If, as an alternative, we regard the biosphere as a whole, certain resemblances, or at least analogies, become apparent between the two approaches. Both the biosphere and the individual organisms that live in it are bathed in a stream of energy. The earth receives solar radiation in the daytime and emits radiation of longer wavelength to outer space at night. In an analogous fashion a living cell continually takes in nutrients as source of energy and excretes products of degradation. Since these nutrients were synthesized by plants at the expense of solar energy, photosynthesis is the point at which a fraction of the energy stream that bathes our planet is channelled away to flow through the biomass. This classical viewpoint is very satisfying, but is concerned with synthesis and maintenance rather than degradation. The latter calls for the perspective we obtain by placing oxygen gas (O_2) at the center of the picture (Dagley 1975b).

The accumulation of O_2 in our atmosphere was a development that made possible the full evolution of living forms in all their present diversity. Any organism that remained anaerobic was handicapped by its inability to take full advantage of the energy gradient that came to be established between biochemicals and carbon dioxide. With O_2 abundant in our atmosphere, the stablest compound of carbon is CO_2. Under these conditions, all terrestial compounds are thermodynamically unstable to varying degrees. All organic compounds found on earth have been synthesized by a living organism, whether the organism was a plant or chemist. The energy released by the ancient, anaerobic process of glycolysis is only a fraction of that made available when glucose is burned to carbon dioxide and water.

However, hazards to life as well as thermodynamic advantages and opportunities are presented by an atmosphere of O_2. Since living forms are made of biochemicals, indiscriminate combustion of these materials must be avoided. Accordingly, if we inspect a map that summarizes central metabolic sequences, we find that oxygen is effectively excluded until such time as the cytochrome chain is ultimately reached and protons and electrons finally combine directly with oxygen to give water.

Before this point is reached, biochemicals have usually been oxidized not by using O_2 but by removing H atoms and transferring them to NAD or NADP. Anaerobic processes analogous to those that operated when life emerged have been preserved in aerobic organisms. However, this apparent exclusion of O_2 from general metabolism simply arises from a fundamental property of the molecule without which the present range of life on earth could not be sustained. This property is the sluggishness shown by oxygen towards organic compounds at physiological temperatures, despite the fact that a great deal of energy is released once the reaction is started and complete combustion is able to occur. Oxygen exists in a triplet ground state: it has two unpaired electron spins and the molecule is paramagnetic. Since carbon in organic compounds is in a singlet state, concerted reactions with oxygen are spin-forbidden; in order to react, oxygen must be "activated" by radiation energy or by specifically combining with an enzyme to attain a singlet state. Haphazard activation would be catastrophic.

The possibility that highly reactive oxygen might gain random access to cellular constituents poses a threat to any form of life; and the apparent ubiquity of the superoxide dismutase in aerobic organisms (McCord et al. 1971) suggests that this enzyme constitutes an essential part of life's defense against the toxicity of oxygen. Strict anaerobes do not possess superoxide dismutase, and die on contact with oxygen. However, although it is extremely hazardous for living matter to activate O_2, it became necessary to catalyze this process on innumerable occasions. This special function is largely reserved for aerobic microorganisms. Without this activation, and the subsequent reactions in degradative sequences that are also catalyzed, the carbon cycle could not function continuously; neither would this planet be cleansed from the contaminating activities of man. A knowledge of these processes forms an indispensable conceptual framework for a biochemical approach to many problems of environmental pollution (Dagley 1975a). We must understand those features of chemical structure that microbial enzymes can or cannot tolerate in molecules presented as substrates, and also study those mutations that might confer increased degradative versatility.

The properties of a number of monooxygenases that prepare aromatic substrates (heterocyclic as well as benzenoid) for ring cleavage, and also of dioxygenases that catalyze this process (Dagley 1971, 1975a), have been reviewed in detail. Their abilities to attack man made organic compounds have also been discussed in the same reviews. Attention will therefore be confined to a few salient observations.

Chemical Structures of Persistent Organic Compounds

The chemical structures of pesticides and of widespread environmental pollutants often contain halogen substituents (usually chlorine), so that superimposed upon the problem of degrading the carbon skeleton of the molecule are additional complications that arise from the introduction of elements encountered rather infrequently in biochemicals. The problem is sometimes approached by first assuming that soil microbes are provided with a biodegradable carbon skeleton such as benzoic acid or a phenol, and then posing the question: How will the introduction of halogen substitutes affect biodegradability? There is good evidence that the benzene nucleus is attacked initially by an electrophilic form of oxygen (Dagley 1975a); and we might therefore expect that substituents such as chlorine, which withdraw electrons from carbon, would render the nucleus less susceptible to attack. Moreover, the more chlorine atoms there are, the greater the deactivation; but probably more important, the greater is the probability that chlorine-containing metabolites, should they be formed, will resist attack by subsequent enzymes. Alexander and his collaborators (Alexander and Lustigman 1966, MacRae and Alexander 1965) have indeed shown that the presence of halogen atoms greatly reduced biodegradability, and have investigated various other effects of molecular structure upon persistence. However, if we attempt to make predictions about the metabolic pathway to be followed, based simply on the probable effects of substituents upon reactivity, we encounter the following uncertainties.

1. The question as to how the degradation of benzoic acid, for example, will be affected by the presence of a chlorine atom at C-4 is not in itself entirely valid, since it is probable that when the halogen is eliminated its place will be taken by hydroxyl, giving 4-hydroxybenzoate. Research on microbial aromatic catabolism has shown that every one of the enzymes employed for the conversion of 4-hydroxybenzoic acid into Krebs cycle metabolites will be different from its counterpart in the pathway used for benzoic acid (Dagley 1975b). The microbial view of chemical structure, if we may so express it, is not that of an organic chemist for whom resemblances reside in carbon skeletons, with substituents of lesser importance. For a microbe faced with a new source of carbon, the insertion of an extra hydroxyl group often entails the elaboration of a whole battery of enzymes to be used in a totally different pathway.

2. Predictions based exclusively on chemical reactivity for nonenzymic systems are not necessarily valid when the reaction is enzyme-catalyzed. For example, fumarase catalyzes the hydration of fluorofumarate to give α-fluoromalate, from which H^+ and F^- ions are immediately expelled to give oxaloacetate (Clarke et al. 1968). This hydration is predicted on purely chemical grounds by Markownikoff's rule. However, chlorofumarate and other halogenofumarates are hydrated the other way around, yielding β-substituted malates, and the halogen is not expelled. The intervention of the enzymes gives an unexpected result--one that cannot be predicted from electron density distributions for molecules not bound to this enzyme (Teipel et al. 1968). Purely chemical considerations might also be evoked to account for the observation that, whereas the benzene nucleus of 4-methylcatechol is oxidatively cleaved between C-2 and C-3, meta fission of 4-carboxycatechol (protocatechuate) by pseudomonads occurs between C-4 and C-5 (Dagley 1975b). However, such considerations would not explain why a dioxygenase recently isolated from _Bacillus circulans_ differs from those from pseudomonads in cleaving the same substrate, protocatechuate, between C-2 and C-3 (Crawford 1975).

3. To treat the degradation of a halogen-substituted compound exclusively in terms of the known reaction pathway for the unsubstituted parent compound is to ignore the possibility that enzymes may exist whose natural substrates contain carbon-halogen bonds. Because such compounds do not participate in the central metabolic cycles

and sequences of biochemistry, the halogen atoms must be eliminated before these points are reached in degradative routes. Will this elimination be fortuitous; i.e., will the halogen be released by an enzyme that does not normally function for that purpose? Or will this be achieved by an enzyme especially evolved for elimination? Clearly, since pesticides are made by man and not by nature, the enzyme is not likely to be tailored to accommodate groups around the particular carbon-halogen linkage under consideration.

It appears that natural halogenated organic compounds are more abundant and much more widely distributed than was once supposed. Thus although only about 30 organic compounds containing chlorine were characterized in 1968 as natural products (Fowden 1968), a review of Siuda and De Bernardis (1973) lists more than 200 naturally-occurring compounds with carbon-halogen bonds, and about 150 of them contain chlorine. Recent surveys of natural products found in marine environments (Hager et al. 1976) indicate that many new compounds, especially those containing bromine, will shortly be added to the list. It is therefore probable that many bacterial enzymes remain to be discovered that have been evolved specifically for the purpose of releasing halogens bound to carbon.

It is important to study the degradation of naturally-occurring compounds containing halogen atoms and to examine the substrate specificities and modes of action of the enzymes involved. Apart from the work of Goldman (1972) on fluoroacetate and related compounds, some of which are found in nature, this area has been neglected. And yet it would be much more profitable to elucidate the enzymology of halogen elimination for biodegradable natural products than to follow the present trend of accumulating empirical data for compounds that were selected for their toxic action upon pest species. The microbial catabolism of chlorophenoxyacetic acid is one of the few areas that can be cited as providing a thorough biochemical investigation of chlorine-containing pesticides (Tiedje et al. 1969, Evans et al. 1971). It is significant that these studies indicate that a specific (or nonfortuitous) process operates for chlorine elimination. Bacteria grown with chlorophenoxyacetic acids were found to oxidize the growth substrate more readily than chlorine-free analogs. Moreover, a lactonizing enzyme that eliminates chloride ion differed in several of its properties from the enzyme that lactonizes an analogous chlorine-free substrate.

Microbial Degradation of Aromatic Compounds

Despite the fact that many years ago Gray and Thornton (1928) conducted an extensive investigation in which soil bacteria of many types were identified that could grow at the expense of aromatic compounds, the mistaken view has gained acceptance that this capability is restricted to a few genera such as *Pseudomonas*, *Arthrobacter*, or *Acinetobacter*. This is largely due to the fact that enrichment procedures for isolating such bacteria tend to select only those that grow rapidly. Vigorous growth of a pure strain in mineral salts medium is a great advantage in biochemical studies, but it does not necessarily encompass all of the most important features of a natural habitat. Moreover, studies of microbial ecology are as important as those concerned with biochemistry. Mixed populations of microorganisms will develop where soil or water is polluted, and it is very desirable to identify these organisms and to understand their nutritional relationships. Thus, a compound such as cyclohexane may be readily metabolized in soil despite the fact that single microbial species capable of using the compound as sole source of carbon are very rarely isolated. It appears that some organisms can oxidize the paraffin only as far as cyclohexanone, and that this serves as a growth substrate for others (Beam and Perry 1974). In a mixed population, therefore, one type of organism might partially metabolize a compound without deriving any obvious benefit, but in so doing it may furnish a suitable growth substrate for a second type. This situation may be described as "commensalism". Alternatively, a compound may fail to induce in a *single species* the enzymes required for its own degradation. The presence of a second compound may be needed to act as derepressor, or to serve as a source of energy required for new enzyme synthesis. For example, certain hydrocarbons do not support the growth of *Pseudomonas methanica* but are partially oxidized by cultures employing methane. Leadbetter and Foster, who made these observations in 1959, described this behavior as "cooxidation"; thus methane supported the cooxidation of *n*-butane to *n*-butanol, *n*-butyric acid and 2-butanone (Leadbetter and Foster 1959, Foster 1962). More recently the term "cometabolism" has been proposed to cover the many instances when a partially-metabolized compound fails to serve as a growth substrate (Horvath and Alexander 1970, Horvath 1972). In another context, the metabolism of one substrate might provide a reduced coenzyme needed to initiate attack upon a second. Thus, the degradation of lignin by aerobes almost certainly requires the investment of a large amount of energy (as reduced pyridine nucleotides) in order to initiate attack upon carbon-carbon and ether linkages that are resistant to all degradative enzymes except oxygenases. It appears that the energy and reduced cofactors for oxygen activation may be provided by the simultaneous degradation of cellulose that is found in natural association with lignin (Kirk et al. 1976).

The Importance of Degradation to Mineral Forms

Bacterial action may not be beneficial unless complete mineralization of an organic pollutant occurs. Intermediate products may be formed that are far more harmful than the original compound. Examples have been provided in a review by Kearney and Kaufman (1972). Thus, concern has been expressed over the nature of several aniline condensation products that arise from 3,4-dichloroaniline (DCA) during the metabolism of the herbicide propanil in soils. Propanil is one of the major herbicides used to control certain grasses (*Echinocloa crusgalli*) in rice (*Oryza sativa*). The propanil controversy began when Bartha and Pramer (1967) reported that soil treated with 2000 ppm propanil produced a major metabolite subsequently identified as 3,3',4,4'-tetrachloroazobenzene (TCAB), which was formed by condensation of two molecules of 3,4-dichloroaniline. Subsequent metabolic studies with the herbicides karsil and dicryl also reported the appearance of TCAB (Bartha et al. 1968). Studies with a large number of chlorinated anilines revealed that all monochloro- and several dichloroanilines were transformed to their corresponding dichloro- and tetrachloroazobenzes in soil (Bartha and Pramer 1967, Bartha et al. 1968). These compounds are structurally related to known potent carcinogens. These observations emphasize the fact that vital information may be missed if studies merely document the slow disappearance of a compound from soil. Careful identification of products by means of modern analytical techniques, supplemented by detailed metabolic studies, is also required.

New Bacterial Strains for Degradation

One of the most significant contributions that could be made to the solution of environmental problems would be the selection of new mutant microbial strains capable of degrading organic compounds that have hitherto appeared to be recalcitrant. Thus, in discussing problems created by persistent pesticides, a recent report to the U.S. Secretary of Agriculture (NRC 1974b) points out that microbes have had at their disposal a time span of billions of years in which to acquire the ability to degrade organic natural products. Organic chemists have been contributing novel substances for only a century or so, and the biosphere has received the products of their ingenuity in significant amounts as pesticides only in the last twenty years. "How long", the report asks, "will it take for microbes to acquire the ability to destroy these compounds?" Evidently, if we are to speculate as to what microbes might be able to accomplish eventually, it would be helpful to have a clear picture as to how they came to acquire their present capabilities. Evolution in the microbial world was the subject of a recent symposium; however, as Hartley (1974) concludes in his contribution: "We are a long way from the systematic molecular anatomy that must underlie any firm opinions about how these molecules (microbial enzymes) evolved". Excellent summaries of speculations relating to these questions are also to be found in the reviews of Clarke (1974) and Hegeman and Rosenberg (1970). The following brief summary outlines experimental approaches. We may consider the example of a novel compound, not normally encountered in nature, which might be metabolized by enzymes employed for a related pathway except that the organism lacks the ability to catalyze the initial reaction(s) that would allow this pathway to be used. Suppose an initial dehydrogenase is lacking. Recent work has shown that suitable mutations may enable a dehydrogenase to be recruited from a different pathway to perform the new function. The earliest work in support of a mechanism of this type was that of Wood and Mortlock and their colleagues, who investigated the growth of various bacterial species with pentoses and pentitols (references to several publications in this area are listed by Clarke [1974]). Let us consider wild type Klebsiella aerogenes that grows with ribitol but not with xylitol, a compound not normally found in nature that fits the description of a novel substrate. One obstacle to growth is that xylitol is not able to derepress enzymes involved in its own metabolism. However, it does serve as substrate for ribitol dehydrogenase, although catalysis is not very efficient because of the low affinity of the enzyme for this alternative substrate (Km for ribitol is about 1 mM; that for xylitol is about 1 M). Slow growth with xylitol might therefore be possible for cells that contained an adequate level of dehydrogenase, provided this could be obtained without the necessity of derepression, for this enzyme converts xylitol into D-xylulose, a compound that is used efficiently by these organisms. This freedom from the constraints of inducer specificity can be achieved by isolating "constitutive mutants" that can produce large amounts of enzymes, 2 percent or more of the total cell protein, in the absence of any inducer. This is the most common mutation studied that permits the use of a novel substrate, whether it be a pentitol or one of a series of amides investigated by Clarke and her colleagues (1974). By using a variety of different amides in selection media, these workers selected additional mutants having amidases with altered substrate specificities compared with the wild type *Pseudomonas aeruginosa*. Accordingly, these mutants grew at the expense of amides that the parent organisms could not use. Wu et al. (1968) selected mutants of *K. aerogenes* possessing the new characteristic of being able to grow with xylitol by isolating first a mutant constitutive for ribitol dehydrogenase (RDH), and from this a second mutant that possessed an altered RDH with an increased affinity for xylitol. As a result of a third mutation, the xylitol was transported more rapidly into the cell, apparently by means of an active transport system that was produced constitutively, and although used by the wild type to transport D-arabitol, could also accommodate xylitol.

Hartley and his colleagues (Rigby et al. 1974) have taken a different approach to studying the part played by RDH in enabling *K. aerogenes* to grow with xylitol as carbon source. A strain constitutive for RDH was again used, but growth now took place in a chemostat, so that measurements of the steady state biomass and the concentration of xylitol in the effluent could be used to signal the appearance of spontaneous mutants able to use the carbon source more effectively. It appeared that, under these conditions, this result was achieved simply by the mutants making more and more enzyme, rather than by producing RDH with a stronger affinity for xylitol. Thus, extracts made from cells taken at appropriate time intervals from the chemostat contained, respectively, 2, 9, and 32 units of RDH/mg of extract protein, but the Km for xylitol was about the same for each, namely 1.3 M. From these observations and many others made by this group, it is clear that mutations leading to increased production of enzyme occurred much more frequently than those leading to improved enzyme specificity. In this particular system it is probable that multiplication of the RDH gene occurred in some mutants, and was reflected in increased enzyme production, and that any mutations to give improved specificity would be acceptable only in "silent gene" copies. It should be mentioned that the mutant with increased specificity for xylitol, used by Wu et al. (1968), was obtained by powerful nitrosoguanidine mutagenesis, and not by use of a chemostat as described by Rigby et al. (1974).

A start has been made, therefore, on delineating mutational events and their enzymic consequences that can result in the ability of microorganisms to degrade novel compounds. These findings will serve as guidelines for experiments with, say, aromatic compounds, which are more directly related in chemical structure to many environmental pollutants than are the pentitols and amides mentioned. No systematic studies in this area have been reported so far, but it is clearly important that they should be attempted. It is a fortunate circumstance that phenols, cresols, xylenols, and various aromatic hydrocarbons, the products of petroleum and coal-based industries, are all metabolized by various suites of microbial enzymes without the prior requirement of mutational events. The reasons that these compounds can be accommodated by wild-type organisms emerged when catabolic pathways were established and substrate specificities of enzymes were determined (Dagley 1975a). Studies of various enzyme sequences of aromatic catabolism also appear to be able to furnish an approach to the problem of determining the mechanisms by which pathways evolved. Thus, Ornston and his colleagues (see Dagley 1975a) have purfied the various enzymes that degrade catechol (1,2-dihydroxbenzene) and protocatechuic acid (4-carboxy-1,2-dihydroxybenzene). These two compounds are degraded by very similar chemical reactions, but the individual enzymes are entirely distinct proteins. Comparisons of enzyme structures, when these have been determined completely, will reveal structural similarities and should suggest evolutionary affinities. Thus one question to answer would be: are analogous reactions catalyzed by enzymes of very similar structure? If so, it might be inferred that "recruitment" of an enzyme from one pathway to function in another could have occurred in the past. Another rapidly developing area of microbial genetics concerns the role of plasmids in disseminating genetic information throughout bacterial populations. In several species, plasmids are now known to carry the genetic information for sections of aromatic catabolic pathways. Moreover, workers on the metabolism of 2,4-D and related herbicides find, not infrequently, that freshly isolated bacteria may rapidly lose their initial ability to grow at the expense of these compounds. One may surmise that plasmids may have a more positive influence in determining the abilities of strains to degrade pesticides than has hitherto been recognized; conversely, as strains lose their plasmids, so they may fail to degrade the man-made compound in question.

Bioaccumulation of Synthetic Organic Compounds

The chemical and physical properties of synthetic materials provide the clues to an evaluation of the hazards that they pose to the environment and to our health. Important properties include volatility, water and lipid solubility, number and location of function groups, and configuration of the carbon skeleton. These properties vary greatly among synthetic organic compounds and largely determine the extent to which a compound may be bioaccumulated.

The process of bioaccumulation involves several events, such as: (a) partitioning between the environment and some surface of the organism, (b) diffusional transport across cell membranes, (c) transport mediated by body fluids, such as exchange between blood vessels and serum lipoproteins, (d) concentration in various tissues depending upon upon affinity for certain biomolecules, such as nerve lipids, and (e) biological modification, or complete or partial biological degradation of the foreign material. The kinetics of each event vary according to the chemical and physical properties of the compound involved. The extent to which bioaccumulation occurs in an organism depends upon the equilibrium concentration, which results from a balance among rates of uptake by diffusion and transport, and rates of removal by catabolic or elimination processes.

Physical processes (passive transport) seem to be the most important mechanisms in the biological uptake of synthetic compounds. An understanding of the mechanism of carcinogenesis by polynuclear aromatics is in part limited by lack of knowledge of the passive processes for the transport of compounds into cells. Polynuclear aromatics are activated in the liver and in cell lysosomes to give arene oxides, which are probably the carcinogenic forms of these compounds (Jerina and Daly 1974). It appears likely that these molecules must migrate to the nucleus prior to degradation if a neoplastic growth is to be induced. Due to low water solubility, these molecules most likely bind to cell proteins and are then exchanged into the nuclear membrane. Diffusion across this membrane is then necessary. Thus, passive transport properties are a highly important area of study for a wide variety of synthetic organic molecules.

Mechanisms for uptake by active transport have not evolved for many synthetic molecules. However, it is likely that existing transport systems that are meant for other purposes are important in the uptake of many synthetic organic compounds. For example, xylitol--a synthetic compound--is known to be transported by the transport mechanism for D-arabitol (Wu et al. 1968). The serum lipoproteins of aquatic and mammalian species effect the uptake and transport throughout an organism of triglycerides and membrane components, cholesterol and its esters, and phospholipids (Nichols 1969, Brown et al. 1975, Hobbelen et al. 1975), and may also effect the uptake and transport of xenobiotic compounds.

Uptake and transport of small synthetic molecules such as pesticides, polychlorinated biphenyls (PCBs), and methyl mercury, is presently of great interest as a result of the need to explain their bioaccumulation and environmental transport in higher organisms. Such transport and accumulation have been observed on many occasions. For example, high levels of PCBs were found in both freshwater and marine organisms (Ahmed 1976), and DDT has been detected in birds and fish at concentrations much higher than those in their environment or in the food they consume (Stickel 1973).

It appears likely that many toxic effects result from interactions between the synthetic compounds and biological membranes. General and local anaesthetics probably function as a result of their interactions with membranes and their effects on membrane function. The symptoms of exposure to chlorinated hydrocarbon pesticides indicate some interference with the functioning of both the peripheral and central nervous systems. To date, no mechanism of action has been elucidated for either anaesthesia or for the pesticidal activity of chlorinated hydrocarbons. Stability and low water solubility alone do not sufficiently explain the insecticidal activities or bioaccumulation. Figure C.2 compares these properties for three similar molecules. It shows that DDE bioaccumulates as readily as DDT, but is not an active insecticide (Melnikov et al. 1971). The trifluoromethyl derivative of DDT neither bioaccumulates nor shows insecticidal activity (Kirkwood and Phillips 1946).

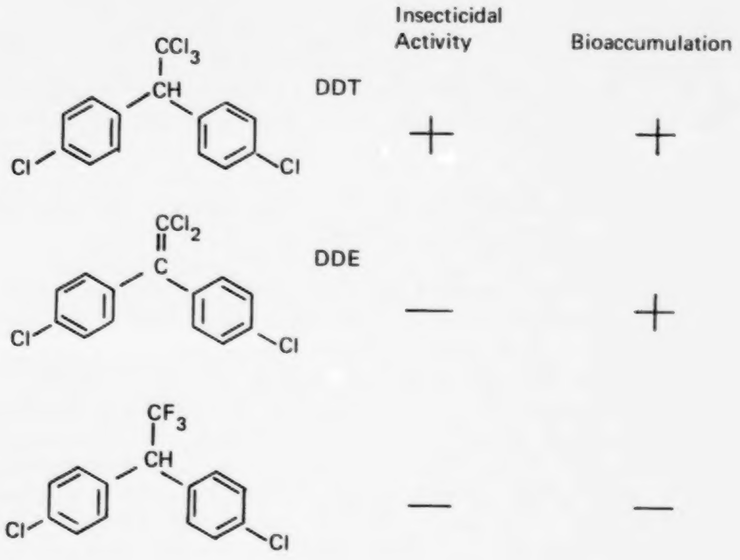


FIGURE C.2 Comparison of the Bioaccumulation Potential and Insecticidal Activity of DDT and Two Analogs

Hexachlorocyclohexane can exist as eight possible steroisomers. The γ isomer (lindane) is the most active, by factors ranging from 50 to 10,000 over the others. These facts indicate the likelihood of specific interaction between synthetic compounds and nerve lipids.

It would be valuable to develop techniques that could reveal the interactions between synthetic molecules and membrane components. By the use of model membrane systems and modern instrumental techniques such as high resolution nuclear magnetic resonance spectroscopy and fluorescence spectroscopy, one can hope to elucidate these specific interactions.

SYNTHETIC ORGANIC CHEMICALS USED IN PEST CONTROL

Special mention of synthetic organic chemicals used in pest control is given here due to the specific methods of application used. Emphasis has been placed on additional areas where research must be concentrated because of the methods of introduction to the environment. Pest control chemicals are to a large extent applied to plants or directly to soils for soil pest control. A major portion of the applied chemicals find their way into soils--complexes of various biological systems--that support plant growth. Contamination of these soils with pesticides may result in contamination of plants with pesticide residues and/or their metabolites. It is essential to determine the fate of pesticides after they have been used and to determine in what amounts, in what form, and under what conditions the pesticides find their way into water, crops, and ultimately into animal and human bodies. A better understanding of factors affecting pesticide-soil-plant interrelationships will, it is hoped, lead to a better usage of agricultural chemicals, and ultimately to a better environment. Continuation of our fight against pests of agricultural and medical importance will necessitate an awareness of the side-effects and ultimate fate of the pest control chemicals that we are introducing into the environment. Since under actual conditions, particularly in agricultural situations, a mixture of synthetic chemicals and/or their metabolites is present, it is possible for these chemicals to interact in biological systems.

Some pesticides are bound, and the presence of other chemicals may affect the persistence or toxic effects of any particular compound under investigation. Disappearance, or lack of persistence, is not necessarily synonymous with degradation. A compound may be sorbed on particles until the reservoir is saturated. By this means the pesticide, though out of sight and mind, has merely been swept under the carpet (NRC 1974b). It is also feasible that since adsorption is a prerequisite for catalytic action, the compound may well undergo partial, nonbiological degradation and may not be sequestered in its original form. Products of partial microbial degradation may also be sequestered in this way.

Since the introduction of synthetic chemicals for agricultural pest control, difficult problems have emerged relative to the fate of these materials after they have been used (Katan et al. 1976). Because of the limited availability of analytical methods between 1945 and 1962, and the initially restricted knowledge about the metabolism of many pesticides, analyses during those years consisted primarily of measuring the concentration of the applied pesticide in extracts of soil, plant tissue, and so forth. The resulting data, often published as depletion curves, have been used to indicate the persistence, disappearance, or loss of pesticides. The possibility that some fraction of the original pesticide might not be extractable after application to plants and soils was generally not considered in explanations of the observed loss or disappearance. It was only when techniques using radiolabelled compounds were applied in studies of pesticide uptake and metabolism that it was possible to detect unextracted radioactivity remaining in the extracted soils. Determining the nature of the radiolabelled compounds (whether original unextracted pesticide, degradation product, or atoms removed from the pesticide and incorporated into natural compounds such as sugars, amino acids, etc.) is complicated since current methods for their detection (combustion, hydrolysis) also result in their destruction. Elucidation of the mechanism for the adsorption of pesticides to soils could possibly clarify the nature of pesticides in soils and their potential for release. It is possible that some nonpersistent pesticides endure longer than we thought, although the nature of the adherence to soil particles is not yet known. Furthermore, what conditions might cause the re-release of these pesticides to the environment, and what might be their chemical form and potential biological activity?

With regard to these questions the following areas of research are important:

1. The rate of formation of nonextractable pesticide associations with soil particles, plant tissues, etc.

2. Effects of environmental conditions on the rate of pesticide adsorption.

3. Factors responsible for the formation of such associations with various substrates.

4. Elucidation of the nature of the nonextractable pesticide sorption.

5. Factors that could affect the release of pesticides.

6. Establishment of the biological activity, if any, of these released pesticides.

Although it is imperative to study the fate and behavior of single environmental chemicals, it is also apparent that these problems must be approached within the concept of a whole system in which chemicals can interact with each other. In particular the following areas of research should get increased attention:

1. Effects of mixtures of pesticides on enzyme systems that degrade and detoxify a particular agricultural chemical.

2. Effects of mixtures of pesticides on the uptake and metabolism of a particular agricultural chemical in food plants, animals, soils, and so forth.

SPECIFIC RECOMMENDATIONS

From the above discussion of the environmental transport and transformation of synthetic organic chemicals the following needs for research emerge:

1. Through the use of the cycle approach, it is recommended that synthetic organic compounds be evaluated and tested for persistence and for bioaccumulation potential. Further studies must be conducted to determine the relationships between physical and chemical properties of synthetic organic compounds and the way these properties influence the behavior of the chemicals in the environment.

2. More research is needed on passive transport processes to determine the kinetics of diffusion and the partition of individual compounds. Once this information is obtained for a group of compounds with different chemical structure, it should be possible to predict rates of bioaccumulation for individual compounds as they are manufactured and released.

3. Delineation of photochemical reactions with synthetic compounds must be made to determine whether

photochemical products are more or less toxic than the parent synthetic compound.

4. A biochemical approach to biodegradability should be adopted, together with the selection of mutants that show increased degradative versatility toward synthetic compounds. Studies to determine the range of microbial species having important biodegradative ability should be extended, with a view to surveying organisms in the laboratory followed by validation of their metabolic ability in the field.

5. A study of the degradation of natural products that contain halogen substituents should help us to obtain more knowledge of dehalogenation reactions for synthetic compounds which contain chlorine.

6. Studies to determine persistent and toxic chemical species that may arise from bacterial modification of pollutants are of critical importance.

7. We must investigate the possibilities of designing pesticides and insecticides that more closely resemble natural products that are degraded by microorganisms in the biosphere. Special emphasis should be placed on oxidative degradation, since this process leads to complete mineralization of the compound concerned.

8. Increased research emphasis must be placed on the environmental fate of combinations of compounds, and the ways in which interactions among these compounds influence their transport and transformation.

9. Studies are needed of interactions of pesticides with soil particles, particularly to determine the importance of sorption processes to chemical persistence.

REFERENCES

Acree, F., M. Beroza, and M.C. Beroza (1963) Codistillation of DDT with water. Journal of Agricultural and Food Chemistry 11:278-280.

Ahmed, A.K. (1976) PCBs in the environment. Environment 18(2):6-16.

Alexander, M. and B.K. Lustigman (1966) Effect of chemical structure on microbial degradation of substituted benzenes. Journal of Agricultural Chemistry 14:410-413.

Anderson, D.W. and J.J. Hickey (1976) Dynamics of storage of organo-chlorine pollutants in herring gulls. Environmental Pollution 10:183-200.

Bartha, R. and D. Pramer (1967) Pesticide transformation to aniline and azo compounds in soil. Science 156:1617-18.

Bartha, R., H.A.B. Linke, and D. Pramer (1968) Pesticide transformations: production of chloroazobenzenes from chloroanilines. Science 161:582-583.

Beam, H.W. and J.J. Perry (1974) Microbial degradation of cycloparaffinic hydrocarbons via cometabolism and commensalism. Journal of General Microbiology 82:163-169.

Brown, M.S., J.R. Faust, and J. L. Goldstein (1975) Role of the low density lipoprotein receptor in regulating the content of free and esterified cholesterol in human fibroblasts. Journal of Clinical Investigation 55:783-793.

Cahn, R., R. Phipers, and E. Brodaty (1945) Stability of derris in insecticidal dusts: The solvent-powder effect. Journal of the Society of Chemical Industry 64:33-35.

Chen, Y.L. and J.E. Casida (1969) Photodecomposition of pyrethrin 1, allethrin, phalthrin and dimethrin. Modifications in the acid moiety. Journal of Agricultural Food Chemistry 17:208-215.

Clarke, D.D., W.J. Nicklas, and J. Palumbo (1968) Fluoromalate: a substrate for fumarate hudratase. Archives of Biochemistry and Biophysics 123:205-215.

Clarke, P.H. (1974) The evolution of enzymes for the utilization of novel substrates. Pages 183-217, Evolution in the Microbial World, edited by M.J. Carlile and J.J. Skehel. Symposium of the Society for General Microbiology, no.24. London: Society for General Microbiology.

Crawford, R.L. (1975) A novel pathway for degradation of protocatechuic acid in a species of Bacillus. Journal of Bacteriology 121:531-536.

Crosby, D.G. (1972) Environmental photooxidation of pesticides. Pages 15-23, Degradation of Synthetic Organic Molecules in the Biosphere. National Research Council. Washington, D.C.: National Academy of Sciences.

Dagley, S. (1971) Catabolism of aromatic compounds by microorganisms. Advanced Microbial Physiology 6:1-46.

Dagley, S. (1975a) A biochemical approach to some problems of environmental pollution. Essays in Biochemistry 11:81-138.

Dagley, S. (1975b) Microbial degradation of organic compounds in the biosphere. American Scientist 63:681-689.

Enderson, J.H. and D.D. Berger (1968) Chlorinated hyrdocarbon residues in peregrines and their prey species from Northern Canada. Condor 70:149.

Evans, W.C., B.S.W. Smith, H.N. Fernley, and J.I. Davies (1971) Bacterial metabolism of 2,4-dichlorophenoxyacetate. Biochemical Journal 122:543-551. (Other relevant papers are in the same volume, pages 509, 519, and 533.)

Foster, J.W. (1962) Bacterial oxidation of hydrocarbons. Pages 241-271, Oxygenases, edited by O. Hayaishi. New York: Academic Press.

Fowden, L. (1968) The occurrence and metabolism of carbonhalogen compounds. Proceedings of The Royal Society 171:5-18.

Frawley, J.P., J.W. Cook, J.R. Blake, and O.G. Fitzhugh (1958) Effect of light on chemical and biological properties of parathion. Journal of Agricultural and Food Chemistry 6:28-30.

Goldman, P. (1972) Enzymology of carbon-halogen bonds. Pages 137-146, Degradation of synthetic organic molecules in the biosphere. National Research Council. Washington, D.C.: National Academy of Sciences.

Gray, P.H.H. and H.G. Thornton (1928) Soil bacteria that decompose certain aromatic compounds. Centralblatt fur Bakteriologie Parasitenkunde and Infektionskrankheiten 73:74-96.

Hager, L.P., R.H. White, P.F. Hollenberg, D.L. Doubek, R.C. Brusca, and R. Guerrero (1976) A survey of organic halogens in marine organisms. Proceedings of the 4th International Food-Drugs from the Sea Conference, November, 1974, Myaguez, Puerto Rico. In press.

Hartley, B.S. (1974) Enzyme families. Pages 151-182, Evolution in the Microbial World, edited by M.J. Carlile and J.J. Skehel. Symposium of the Society for General Microbiology, no. 24, London: Society for General Microbiology.

Hegeman, G.D. and S. L. Rosenberg (1970) The evolution of bacterial enzyme systems. Annual Review of Microbiology 24:429-462.

Hobbelen, P.M.J., A.C. Coert, J.A.A. Geelen, and J. van der Vies (1975) Interactions of steroids with serum lipoproteins. Biochemical Pharmacology 24:165-172.

Horvath, R.S. (1972) Microbial co-metabolism and the degradation of organic compounds in nature. Bacteriology Review 36:146-155.

Horvath, R.S. and M. Alexander (1970) Co-metabolism: A technique for the accumulation of of biochemical products. Canadian Journal of Microbiology 16:1131-1132.

Jerina, D.M. and J.W. Daly (1974) Arene oxides a new aspect of drug metabolism. Science 185(4151):573-582.

Jones, H.A. and H.L. Haller (1931) The "yellow compounds" resulting from the decomposition of rotenone in solution. Journal of the American Chemical Society 53:2320-2324.

Katan, J., T.W. Fuhremann, and E.P. Lichtenstein (1976) Binding of [^{14}C] parathion in soil: a reassessment of pesticide persistence. Science 193(4256):891-894.

Kearney, P.C. and D.D. Kaufman (1972) Microbial degradation of some chlorinated pesticides. Pages 166-189, Degradation of Synthetic Organic Molecules in the Biosphere. National Research Council. Washington, D.C.: National Academy of Sciences.

Kirk, T.K., W.J. Connors, and J.G. Zeikus (1976) Requirement for a growth substrate during lignin decomposition by two wood-rotting fungi. Applied and Environmental Microbiology 32:192-194.

Kirkwood, S. and P.H. Phillips (1946) The relationship between the lipoid affinity and the insecticidal action of 1,1-bis (p-fluorophenyl) 2,2,2-trichloroethane and related substances. Journal of Pharmacology 87:375-381.

Leadbetter, E.R. and J.W. Foster (1959) Oxidation products formed from gaseous alkanes by the bacterium Pseudomonas methanica. Archives of Biochemistry and Biophysics 82:491-492.

MacRae, I.C. and M. Alexander (1965) Microbial degradation of selected herbicides in soil. Journal of Agricultural and Food Chemistry 13:72-76.

McCord, J.M., B.B. Keel, and I. Fridovich (1971) An enzyme-based theory of obligate anaerobiosis: The physiological function of superoxide dismutase. Proceedings of the National Academy of Sciences 68:1024-1027.

Melnikov, N.N., F.A.Gunther, and J.A. Gunther, eds. (1971) Chemistry of Pesticides. New York: Springer Verlag.

Metcalf, R.L., I.P. Kapoor, and A.S. Hirwe (1972) Development of persistent biodegradable insecticides related to DDT. Pages 244-259, Degradation of Synthetic Organic Molecules in the Biosphere. Washington, D.C.: National Academy of Sciences.

Nash, R.G. and M.L. Beall, Jr. (1970) Chlorinated hydrocarbon insecticides: Root uptake versus vapor contamination of soybean foliage. Science 169:1109-1111.

National Research Council (1974a) Accumulation of Nitrate. Committee on Nitrate Accumulation. Washington, D.C.: National Academy of Sciences.

National Research Council (1974b) Productive Agriculture and a Quality Environment. Committee on Agriculture and the Environment. Washington, D.C.: National Academy of Sciences.

Nichols, A.V. (1969) Functions and interrelationships of different classes of plasma lipoproteins. Proceedings of the National Academy of Sciences 64:1128-1137.

Persson, B. (1972) DDT content of white throats, lower after summer stay in Sweden. Ambio 1(1):34-35.

Rigby, P.W.J., B.D. Burleigh, and B.S. Hartley (1974) Gene duplication in experimental enzyme evolution. Nature 251:200-204.

Rosen, J.D. and D.J. Sutherland (1967) The nature and toxicity of the photo-conversion products of aldrin. Bulletin of Environmental Contamination Toxicology 2:1-9.

Siuda, J.F. and J.F. DeBernardis (1973) Naturally occurring halogenated organic compounds. Lloydia 36(2):107-143.

Stickel, L.F. (1973) Pesticide residues in birds and mammals. Chapter 7, Environmental Pollution by Pesticides, edited by C.A. Edwards. New York: Plenum Press.

Tarrant, K.B. and J. O'G. Tatton (1968) Organo-pesticides in rainwater in the British Isles. Nature 219:725-272.

Taylor, B.F., W.L. Campbell, and I. Chinoy (1970) Anaerobic degradation of the benzene nucleus by a facultatively anaerobic microorganism. Journal of Bacteriology 102:430-437.

Teipel, J.W., G.M. Hass, and R.L. Hill (1968) The substrate specificity of fumarase. Journal of Biological Chemistry 243:5684-5693.

Tiedje, J.M., J.M. Duxbury, M. Alexander, and J.E. Dawson (1969) Pathway of degradation of chlorocatechols by Arthrobacter sp. Journal of Agricultural and Food Chemistry 17:1021-1026. (Other relevant papers by this group are in the same volume, page 1080, and in volume 16, page 829.)

Wu, T.T., E.C.C. Lin, and S. Tanaka (1968) Mutants of Aerobacter aerogenes capable of utilizing xylitol as a novel carbon source. Journal of Bacteriology 96:139, 447-456.

Yates, M.L., W. Holswade, and A.L. Higer (1970) Pesticide residues in hydrobiological environments. 159th National Meeting of the American Chemical Society, Water, Air and Waste Chemistry Section. Houston, Texas: Washington, D.C.: American Chemical Society.

BIBLICLOGRAPHY

Bankowska, J. and A. Bojanowska (1972) Detoxification of organophosphorus insecticide following enzymatic induction caused by urea herbicides, Roczniki Panstwowego Zakladu Higieny 23(4):487-493.

Blumenthal, H. (1975) Testimony of PCBs in Paper Food Packaging Materials. Docket No. 75 N-0013. Washington, D.C.: U.S. Food and Drug Administration.

Bollag, J.M. and K.C. Liu (1974) Effect of methylenedioxyphenyl synergists on metabolism of carbaryl by Aspergillus terreus. Experientia 30(12):1374-1375.

Chadwick, R.W. and J.J. Freal (1972) Comparative acceleration of lindane metabolism to chlorophenols by pretreatment of rats with lindane or with DDT and lindane. Food and Cosmetics Toxicology 10(6):789-795.

Chadwick, R.W. and J.J. Freal (1974). Comparative lindane metabolism and enzyme induction in rats pretreated with eight different chlorinated pesticides. Toxicology and Applied Pharmacology 29(1):127.

Conney, A.H. and J.J. Burns (1972) Metabolic interactions among environmental chemicals and drugs. Science 178(4061):576-586.

Dikshith, T.S.S., K.K. Datta, and P. Chandra (1974) Interaction of lindane and diazinon on the skin of rats. Experimental Pathology 9(4):219-224.

DuBois, K.P. (1972) The interaction of environmental chemicals with drugs. Drug Information Journal 6(1):53-58.

El-Refai, A.R. and M. Morvafy (1973) Interactions of propanil with insecticides absorbed from soil and translocated into rice plants. Weed Science 21:246-248.

Fuhremann, T.W. and E.P. Lichtenstein (1972) Increase in the toxicity of organophosphorus insecticides to house flies due to polychlorinated biphenyl compounds. Toxicology and Applied Pharmacology 22: 628-640.

Hamill, A.S. and D. Penner (1973) Butylate and carbofuran interaction in barley and corn. Weed Science 21(4):339-342.

Hamill, A.S. and D. Penner (1973) Interaction of alachlor and carbofuran. Weed Science 21:330-335.

Iyengar, L., M.P. Pandey, C. Venkobachar and A.V.S.P. Rao (1972) Biochemical evaluation of pesticides. Biochemical Journal 128(1):39-40.

Liang, T.T. and E.P. Lichtenstein (1974) Synergism of insecticides by herbicides: Effect of environmental factors. Science 186:1128-1130.

Lichtenstein, E.P. (1966) Increase of persistence and toxicity of parathion and diazinon in soils with detergents. Journal of Economic Entomology 59(4):985-993.

Lichtenstein, E.P. (1972) PCBs and interactions with insecticides. Environmental Health Perspectives 1:151-153.

Lichtenstein, E.P. and J.E. Casida (1963) Naturally occurring insecticides. Myristicin, an insecticide and synergist occurring naturally in the edible parts of parsnips. Journal of Agricultural and Food Chemistry 11(5):410-415.

Lichtenstein, E.P., K.R. Schulz, T.W. Fuhremann, and T.T. Liang (1969) Biological interaction between plasticizers and insecticides. Journal of Economic Entomolology 62(4):761-765.

Lichtenstein, E.P., K.R. Schulz, and G.T. Cowley (1963) Inhibition of the conversion of aldrin to dieldrin in soils with metyhlenedioxphenyl synergists. Journal of Economic Entomology 56(4):485-489.

Lichtenstein, E.P., T.W. Fuhremann, K.R. Schulz, and R.F. Skrentny (1967) Effect of detergents and inorganic salts in water on the persistence and movement of insecticides in soils. Journal of Economic Entomology 60(6):1714-1721.

Lichtenstein. E.P., T.W. Fuhremann, N.E.A. Scopes, and R.F. Skrentny (1967) Translocation of insecticides from soils into pea plants: Effects of the detergent LAS on translocation and plant growth. Journal of Agricultural and Food Chemistry 15(5):864-869.

Lichtenstein, E.P., T.T. Liang, and B.N. Anderegg (1973) Synergism of insecticides by herbicides. Science 181:847-849.

Lichtenstein, E.P., T.T. Liang, K.R. Schulz, H.K. Schnoes, and G.T. Carter (1974) Insecticidal and synergistic components isolated from dill plants. Journal of Agricultural and Food Chemistry 22(4):658.

Ludke, J.L. (1974) Interaction of dieldrin and DDE residues in Japanese quail (Coturnix coturnix japonica). Bulletin of Environmental Contamination and Toxicology 11(4):297-302.

Mosser, J.L., T.C. Teng, W.C. Walther, and C.F. Wurster (1974) Interactions of PCBs, DDT and DDE in a marine diatom. Bulletin of Environmental Contamination and Toxicology 12(6):665-668.

Nadzhimutdinov, K.N., I.K. Kamilov, and Sh.M. Muzrabekov (1974) Vliyaniye pestitsidov na dlitel'nost' geksenalovogo sna. (Influence of pesticides on the duration of hexobarbital-induced sleep.) Farmakologiya; Toksikologiya (Moskva) 37(5):533-537.

National Research Council (1972) Degradation of Synthetic Organic Molecules in the Biosphere. Proceedings of a Conference, June 12-13, 1971. San Francisco, California. Washington, D.C.: National Academy of Sciences.

Onuma, S. (1971) Studies on toxicity of parathion used with lead arsenate. Hirosaki Medical Journal 23(1):43-55.

Parks, J.P., B. Truelov, and G.A. Buchanan (1972) Interaction of prometryne and phorate on bean. Weed Science 20:89-92.

Putnam, A.R. and D. Penner (1974) Pesticide interactions in higher plants. Pages 73-110, Residue Reviews, Volume 50, edited by F.R. Gunther and J.D. Gunther. New York: Springer Verlag.

Richardson, L.T. (1960) Effect of insecticide-fungicide combination on emergence of peas and growth of damping off fungi. Plant Disease Reporter 44:104-108.

Richardson, L.T. and P.M. Miller (1960) Fungitoxicity of chlorinated hydrocarbon insecticides in relation to water solubility and vapor pressure. Canadian Journal of Botany 38:163-175.

Rumsey, T.S. and J. Bond (1974) Effect of urea, diethylstilbestrol, and type of diet on the distribution of aldrin and dieldrin residues in finished beef heifers. Journal of Agricultural and Food Chemistry 22(4):664-667.

Savage, K.E. and H.W. Ivy (1973) Fluometuron-disulfoton interactions with cotton as affected by soil properties. Weed Science 21:275-278.

Schulz, K.R., T.W. Fuhremann, and E.P. Lichtenstein, (1976) Interaction of pesticide chemicals: Effects of Eptam and its antidote on the uptake and metabolism of ^{14}C-phorate in corn plants. Journal of Agricultural and Food Chemistry 24(2):296-299.

Segall, H.J. and J.M. Wood (1974) Reaction of methyl mercury with plasmalogens suggests a mechanism for neurotoxity of metal-alkyls. Nature 248(5447):456-458.

Sperling, F., H.K.U. Ewenike, and T. Farber (1972) Changes in LD50 of parathion and heptachlor following turpentine pretreatment. Environmental Research 5(2):164-171.

Stevens, J.R., J.J. McPhillips, and R.E. Stitzel (1972) In vitro enhancement of aniline metabolism by paraoxon. Toxicology and Applied Pharmacology 23(2):208-215.

Street, J.C., R.C. Baker, D.J. Wagstaff, and F.M. Urry (1971) Pesticide interactions in vertebrates: Effects of nutritional and physiological variables. Pages 281-302, Insecticide Resistance, Synergism, Enzyme Induction. New York: Gordon and Breach Science Publishers.

Thomas, J.A., L.G. Schein, H.D. Colby, and W.J. Canady (1974) Interaction of dieldrin and parathion on androgen metabolism in the prostate and on hepatic P-450 activity in mice. Pharmacologist 16(2):229.

APPENDIX D

ENTERIC VIRUSES:

EXAMPLES OF BIOLOGICAL POLLUTANTS

More than 100 different enteric viruses are known to appear in the excreta of man and animals (Berg 1973); confirmation of the suspected etiologic role (Blacklow et al. 1972, Kapikian et al. 1973) for acute infectious non-bacterial gastroenteritis would further increase the number.

Enteric viruses replicate only within susceptible host cells. The viral nucleic acid core, which is protected by a surrounding protein coat, controls and directs the host cell to produce virus progeny. Survival is equated with maintenance of infectious capability and integrity of structure, which is ordinarily hardy and permits the virus to endure in a hostile environment. Virus survival capabilities thus allow extensive viral transport within the biosphere, with a capacity for both maintenance and regeneration of infectious potential.

The normal state of viruses in natural environments probably involves some form of adsorption to suspended solids. In sewage, viruses may be encapsulated within fecal material. Virus adsorption to clays, silt, and soil particulates in water may enhance transmission, or result in the deposition of viruses in sediments (Carlson et al. 1968, Schaub and Sagik 1975). Viruses adsorbed to atmospheric soil particulates may be carried over long distances before being transferred to land or water surfaces. Viruses in the adsorbed state seem to be better protected from influences that might diminish the effectiveness of the protective viral protein coat. Adsorption may be the mechanism responsible for long-term survival of viruses in a number Of environments. Table D.1 presents survival times of enteric viruses in various environments.

Infectious diseases caused in humans by various enteric viruses are listed in Table D.2. Clearly, enteric viruses have pathogenic potentials for man that include muscle

TABLE D.1 Survival of Enteric Viruses in Natural Environments

Environment	Survival Time (days)
Atmosphere[1]	0.5-10
Sea or Estuary water	2-130
River Water	26-188
Tapwater	5-168
Soil	25-175
Oysters	6-90
Landfill leachates	76-90
Marine and freshwater sediments	?

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[1] Estimated assuming characteristic survival time for submicron aerosol.

TABLE D.2 The Human Viruses and the Diseases they Cause

Virus Group	Number of Viruses in Each Group	Disease
Enteroviruses		
Polioviruses	3	Poliomyelitis, aseptic meningitis
Coxsackievirus A	24	Aseptic meningitis, herpangia, myocarditis, pleurodynia, fever, congenital heart anomalies, and diabetes?
Coxsackievirus B	6	
Echovirus	34	Aseptic meningitis, respiratory infections, diarrhea and rash
Reoviruses	3	Respiratory infections, diarrhea
Adenoviruses	32	Respiratory, eye infections
Infectious hepatitis	1	Infectious hepatitis
Gastroenteritis viruses	?	Acute infectious nonbacterial gastroenteritis

paralysis and meningitis, as well as heart, upper respiratory tract, eye, liver, and acute gastro-intestinal involvements. Infections range from mild, inapparent infections, to serious central nervous system or vital organ involvement. Coxsackie viruses have been associated with diabetes (Craighead 1975), and herpes viruses (non-enteric) with certain forms of cancer (Biggs et al. 1972). Much remains to be learned about the viral role in the induction of these diseases, but the seriousness of each warrants heightened appreciation of the significance to public health of the presence of viruses in the environment.

Treatment of domestic sewage by conventional primary treatment methods is ineffective for virus removal (Berg 1973, England et al. 1967), and secondary and advanced waste treatment methods are usually necessary to remove significant numbers of viruses (Grabow 1968, Berg 1973, Berg et al. 1968, Gerba et al. 1974). Effectiveness of the common wastewater treatment methods is summarized in Table D.3.

It has been estimated that only one of every 100 to 1000 infections will result in clinical symptoms (Taylor 1974). The infected individual serves literally as a human culture supporting enormous numbers of viral progeny. Concentrations reaching one million virons per gram of feces and 463,000 plaque-forming units per liter of raw sewage have been reported (Gerba et al. 1975).

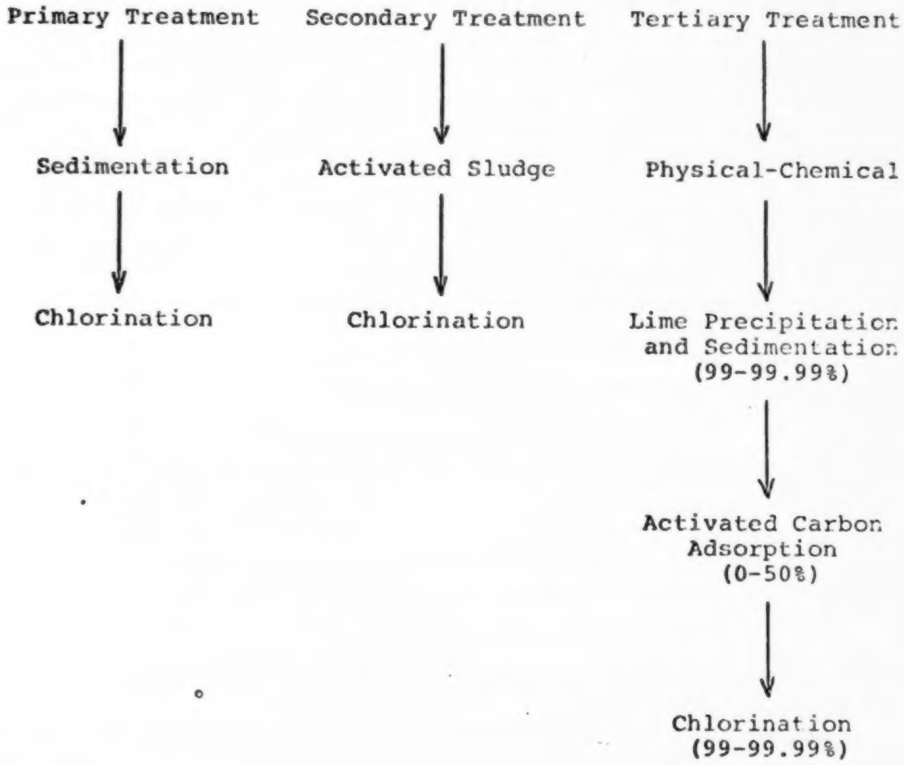
Although it will not necessarily result in clinically recognized illness, one viral plaque-forming unit may be able to infect man (Plotkin and Katz 1965). Therefore, extreme dilution of viruses in the environment may reduce the probability of infection, but will not eliminate it (Westwood and Sattar 1976).

SOURCES OF POLLUTION BY ENTERIC VIRUSES

The source of enteric viruses is the excreta of man and animals. Infectious routes include the following: (a) raw sewage to vegetables to man, (b) man to other persons, (c) sewage aerosols to man (skin or inhalation).

The use of sewage lagooning procedures has consistently failed to remove all of the viruses originally present in influent wastewater (England et al. 1967, Sobsey and Cooper 1973). Sewage lagoon effluents could create a health hazard if discharged into shellfish or recreational waters (Slanetz et al. 1971). There is evidence that surface or underground waters may also be contaminated by release of viruses through leaching action (Cooper et al. 1974).

TABLE D.3 Expected Reduction in Virus Concentration Using Common Wastewater Treatment Methods


Primary Treatment
Sedimentation
Chlorination
Secondary Treatment
Activated Sludge
Chlorination
Tertiary Treatment
Physical-Chemical
Lime Precipitation and Sedimentation (99-99.99%)
Activated Carbon Adsorption (0-50%)
Chlorination (99-99.99%)

SOURCE: Gerba et al. (1975) Reprinted with permission from Gerba, C.P., C. Wallis, and J.L. Melnick (1975) Enteric viruses as biological pollutants. Environmental Science and Technology 9:1122-1126. Copyright by the American Chemical Society.

Pollution of land surfaces may occur following application of sewage wastes, whether for soil enrichment, strip-mined land reclamation, or groundwater recharge purposes. In fact, disposal sites for solid waste have been identified as sources of viruses derived from the use of disposable diapers (Peterson 1974).

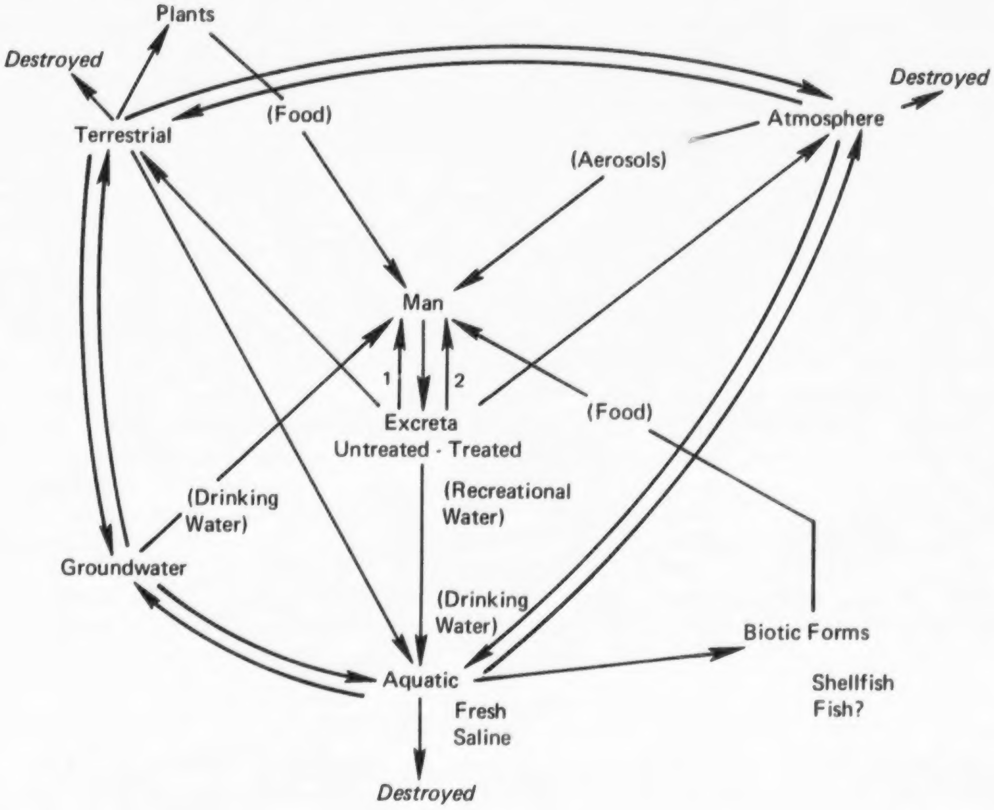
Infectious aerosols produced from, among other sources, waste treatment plants and spray irrigation, have been shown to be one of the most dangerous sources of virus infections (Sorber 1973). The danger associated with these aerosols is related to the degree of penetration into the respiratory tract (Sorber et al. 1972) and the possibility of transmitting viruses over considerable distances from the release point.

PATHWAYS FOR TRANSPORT OF ENTERIC VIRUSES

The major pathways followed by enteric viruses as they pass from point of origin into the environment are shown in Figure D.1. From the original source of human excrement, viruses may be routed to aquatic, terrestrial, or atmospheric environments. Virus interchange may occur between each of these environments. Opportunities for viral inactivation are found in each environment. Human infection may occur through drinking water, recreational water contact, food, and aerosol routes. Little systematic information on infection of man through crop and aerosol routes has been compiled. Information on shellfish and waterborne vectored infections is summarized as follows.

Waterborne

Outbreaks of waterborne disease between 1946 and 1970 are listed in Table D.4. The most startling statistic is the number of cases of gastroenteritis. The number of cases caused by viruses cannot be determined, but if even a fraction were virally induced, their magnitude can be considered substantial, especially in comparison to outbreaks of bacterial and protozoan diseases. A virus etiology may be involved in acute infectious nonbacterial gastroenteritis if the acute infectious nonbacterial gastroenteritis agents are presumed to be viral in nature (Blacklow et al. 1972, Kapikian et al. 1973). A significant feature of the disease outbreak statistics was the evidence of inadequacies in water systems and deficiencies in their operation (DeMichele 1974). Most of the outbreaks were accounted for by use of contaminated springs or groundwater and distribution system contamination through cross-connections and back-siphonage (Craun et al. 1975).


Plants
Destroyed
Terrestrial
(Food)
Atmosphere
Destroyed
(Aerosols)
Man
1
2
Excreta
Untreated - Treated
(Food)
(Drinking
Water)
(Recreational
Water)
Groundwater
(Drinking
Water)
Biotic Forms
Aquatic
Fresh
Saline
Shellfish
Fish?
Destroyed

[1] Man can be exposed to potential infection by direct contact with virus-containing feces.
[2] Man can be exposed to potential infection through the aquatic route.

FIGURE D.1 Enteric Virus Transmission Routes of Public Health Significance

TABLE D.4 Waterborne-Disease Outbreaks: 1946-70, by Type of Illness and System

Illness	Private Systems[1/]		Public Systems[1/]		Total	
	Outbreaks	Cases	Outbreaks	Cases	Outbreaks	Cases
Gastroenteritis	121	8,970	57	36,285	178	45,255
Typhoid	47	507	6	103	53	610
Infectious hepatitis	36	1,094	17[2/]	739	53	1,833
Shigellosis	23	1,616	10	5,784	33	7,400
Salmonellosis	7[3/]	118	6	16,612	13	16,730
Amebiasis	4	50	1	25	5	75
Enteropathogenic E. coli	4	188			4	188
Giardiasis	1	19	2	157	3	176
Leptospirosis			1	9	1	9
Tularemia	2	6			2	6
Poliomyelitis			1	16	1	16
TOTAL	253	12,620	105	59,738	358	72,358

[1/] The terms public and private as used in this table refer not to the ownership of the utility but to the type of service rendered. Generally, public supplies are municipal-type supplies available to all within a certain area. Private supplies include individual and semipublic sources, such as provided by camps, resorts, hotels, industries, and institutions.

[2/] One gastroenteritis outbreak also included seven cases of infectious hepatitis.

[3/] One gastroenteritis outbreak was preceded by outbreak of 38 cases of salmonellosis.

SOURCE: Craun and McCabe (1973) Reprinted from Journal American Waterworks Association Volume 65 by permission of the Association. Copyrighted 1973 by the American Waterworks Association, Inc., 6666 West Quincy Avenue, Denver, Colorado 80235.

Outbreaks of disease caused by waterborne viruses between 1971 and 1974 and their etiology are listed in Table D.5. The data show no reduction in the incidence of outbreaks and support the prediction of a continuance of waterborne disease through the year 1974. Infectious hepatitis is the viral disease of greatest significance when water transmission of viruses is considered (Mosley 1965, U.S. Department of Health, Education and Welfare [USDHEW] 1975), and infectious hepatitis associated with sewage-polluted recreational waters was reported for the first time by Bryan et al. (1974). Waterborne poliomyelitis may be a rare occurrence in the United States; this was substantiated in only one out of eight epidemics (Mosley 1965). Outbreaks of viral disease are most common in private systems, but public systems have most of the cases (Craun and McCabe 1973). The continuing occurrence of waterborne outbreaks makes it essential for regulatory agencies charged with the protection of public health to establish priorities.

Shellfish

Major outbreaks of shellfish-vectored hepatitis have been reported in Sweden and the United States. Cases of the disease followed consumption of polluted oysters in Goteborg, Sweden (Roos 1956), raw clams in Connecticut (Ruddy et al. 1969), sewage-polluted raw oysters in Mississippi and Alabama (Mason and McLean 1962), and fecally contaminated oysters in Georgia (USDHEW 1975). Other outbreaks were reported in New Jersey (Dougherty and Altman 1962) and Texas (USDHEW 1975).

Use of shellfish as fish bait could result in viral contamination of the hands, clothing, or gear of fishermen. Uptake of viruses by shellfish is followed by a passive residence phase. No viral multiplication occurs in shellfish, and the duration of the residence phase depends on feeding activity, physiological vigor of the host and sequestering of viruses in tissue repositories (Metcalf and Stiles 1965).

Enteroviruses were found in marine sediments polluted by sewage discharges from nearshore shallow waters (DeFlora et al. 1975). Such sediments represent a transient reservoir of viruses. Wave motions and bottom currents may be capable of releasing viruses from these sediments. Release of viruses could pose a health hazard for bathers. Ingestion of raw or inadequately cooked shellfish carrying viruses accumulated from a disturbed sediment source represents a potential health hazard.

TABLE D.5 Waterborne Outbreaks and their Etiology, 1971-1974

	1971	1972	1973	1974	Total
Outbreaks	19	29	26	24	98
Cases of Disease	5,182	1,638	1,774	3,329	11,923

Diseases	Outbreaks	Cases
Gastroenteritis	48	9,059
Hepatitis A	13	351
Shigellosis	12	1,507
Giardiasis	11	301
Chemical poisoning	8	447
Typhoid	4	221
Salmonellosis	2	37
TOTAL	98	11,923

SOURCE: Craun et al. (1975) Reprinted from the Journal American Water Works Association Volume 67 by permission of the Association. Copyrighted 1975 by the American Water Works Association, Inc., 6666 West Quincy Avenue, Denver, Colorado 80235.

DETECTION OF VIRUSES

In order to properly conduct research on the fates of viruses, it is necessary to have reliable methods for detecting them. Methods are available for detection of virus in air, water, soil, sewage, foods, and so on. Their effectiveness depends largely upon the type and amount of sample to be examined. The most effective ones are those developed for clean or finished water, where a recovery of 1 to 5 infectious units per 100 gallons can be expected. Recovery procedures for other waters have not been perfected to this degree, and their effectiveness is considerably less. Recovery of viruses from soils is more difficult than recovery of viruses from finished water. Efficiency of viral recovery is low, generally less than 50 percent, and efficiency varies significantly. Although the numbers of viruses in polluted soil may be three or more orders of magnitude greater than the numbers of viruses in equivalent amounts of finished waters, decreased efficiency, limitations of sample size, difficulties in extraction procedures, and so forth result in low yields.

From raw sewage, under optimal conditions, as many as 8 out of every 10 viruses have been recovered from 60-liter samples (Homma et al. 1973). Similar recovery for larger volumes of sewage effluent can be expected on a routine basis. The recovery of enteric viruses from raw, active, or digested sludge is very difficult (Lund 1971, Palfi 1972), and no judgment on efficiency can be made at present.

Test viruses can be detected with reasonable efficiency in foods such as shellfish; recovery efficiencies as high as 70 percent may be achieved in tests using large numbers of viruses (Sobsey et al. 1975). Recovery efficiency is reduced if small numbers of test viruses are used. Only about 3 to 4 of every 10 viruses present in oysters, clams, and mussels can be recovered by present methods (Metcalf 1976).

Root parts yielded the highest recovery of viruses from plants cultivated in virus-polluted soil (Mazur and Paciorkiewicz 1974). Tests showed that recovery was made in 81 percent of the trials from upper root parts, 41 percent of the time from ground parts, and 6 percent from overground green parts.

Rapid methods of testing for viruses in cell culture have been proposed via fluorescent antibody (Katzenelson 1976) or immunoenzymatic (Herrmann and Morse 1973) techniques. Both methods shorten the time required for viral demonstration from weeks to days or possibly hours. However, the immunospecificity of the fluorescent antibody reagent limits testing to one virus at a time. Unless the presence of a specific virus is to be determined, the number of isolation possibilities within the enterovirus group alone presents a technical dilemma. Immunoenzymatic procedures require concentration of viruses and will not distinguish between infectious and noninfectious viruses.

DISINFECTION OF VIRUSES

Removal of viruses from wastewater, including sludge, cannot be guaranteed by treatment using physical and chemical procedures. Disinfection is required to assure virus removal from wastewaters.

Chlorine

The effectiveness of chlorine is influenced by the nature of the chlorine residual (free or combined), presence of organic material, temperature, pH, suspended solids, contact time, and type, number, and condition of biotic forms present (whether adsorbed or aggregated in the case of virus). Thus, treatment by chlorination per se should never be considered proof of disinfection.

Free chlorine is required for significant virus inactivation in sewage (Olivieri et al. 1970). Residuals up to 1 mg/l, maintained for a 30-minute contact period are considered necessary to assure virus-free effluents in turbidity-free water (Berg 1970). Tertiary or advanced waste treatment is usually necessary to eliminate turbidity problems. Although improvements in the terminal disinfection of sewage effluents have been reported (Kruse et al. 1973), application of these methods to sludge is not considered practical. Chlorine is a surface-active element, and under normal conditions of use, incapable of penetrating solid particulates to inactivate embedded viruses. Combined chlorine residuals of 40 mg/l maintained for 30 minutes were required for a 99.99 percent destruction of test poliovirus in settled wastewater (Lothrop and Sproul 1969). Differences in the effectiveness of inactivation for different members of the enteric virus group have been reported (Shuval et al. 1966).

The need for large amounts of chlorine for disinfection of sewage raises problems of expense, production of carcinogenic substances, and toxicity for aquatic forms of life (Zillick 1972, Brungs 1973, Berg 1976).

Ozone

Ozone, although it is a more powerful oxidant than chlorine, is also surface-active and depends upon irreversible oxidation of viral nucleic acid for inactivation effectiveness. Apart from beneficiation leading to increased solids removal and oxidation of organics and nutrient materials, ozonation of sludge for viral disinfection has the same handicaps as chlorination (Majumder and Sproul 1974). Secondary wastewater effluent can be converted to potable water by ozone dosages in excess of 50 mg/l (Kirk et al. 1971). Dosages of this magnitude make ozonation economically unfeasible as a tertiary treatment process at present. The possibility of a more effective inactivation of virus than of bacteria has been indicated (Pavoni and Tittlebaum 1974). Inactivation of 99.99 percent of test Coxsackie virus B3 in water by residuals as small as 0.28 mg/l after 1 minute was indicative of ozone concentrations likely to prove effective in clean water (Keller et al. 1974). Use of ozone for disinfection of potable waters has not received much attention in the United States because the relatively short half-life of ozone (approximately 25 minutes) eliminates any prospect of maintaining an effective residual in water distribution systems.

Lime

Physicochemical treatment of wastewater for removal of solids includes the use of lime at high alkaline values. Treatment with lime under pH conditions higher than 11.0 has been recommended for inactivation of enteric viruses (Berg 1973). At pH greater than 11.0, high percentages of polioviruses were inactivated in less than 90 minutes in domestic sewage (Sattar et al. 1974), and in wastewater (Culp et al. 1973). The use of lime at pH values of 11.5 would be a tertiary or advanced waste treatment method for water renovation. Its extension to virus inactivation in sludge would depend upon costs and availability of appropriate treatment facilities. The high calcium content of lime-treated sludges could influence their use on land surfaces where stimulation of plant growth is contemplated.[1]

Electron Irradiation

Disinfection of viruses in sludge or wastewater by electron irradiation eliminates residual toxicity problems likely to be encountered with chlorination when large treatment dosages are used. Five enteric viruses suspended in wastewater effluents in concentrations of less than 500 PFU were inactivated at 400,000 rads (Metcalf 1975). High-energy electron doses required for inactivation of 15 viruses, including hepatitis, have been estimated at less than 3 million rads (Wright and Trump 1956).

Electron irradiation will inactivate adsorbed as well as encapsulated viruses. Energy costs are greater than the costs of chlorination, but the environmental and ecologic considerations involved in waste management may cancel out this cost advantage.

EXTRAPOLATION OF ENTEROVIRUS MODEL TO OTHER BIOLOGICAL POLLUTANTS

Enterovirus models can be used to predict the behavior and reaction of most bacterial, fungal, rickettsial, chlamydial, and protozoan pathogens to environmental factors. Virus behavior to many physical and chemical influences provides an indicator against which the behavior of other biological pathogens can be estimated. The ability of enteroviruses to provide a frame of reference against which the behavior of other microscopic pollutants can be measured makes them acceptable models for assessing research needs associated with the fate of pollutants released into the environment.

Detailed knowledge on the environmental fates of selected enteroviruses could lead to a better understanding of the control measures needed not only for these few entities, but also for the whole group of enteric viruses (including hepatitis A), as well as for other viral pathogens sharing one or more transmittal routes with the enteroviruses. The ability to control viruses should automatically provide adequate controls for bacteria, fungi, rickettsiae, and chlamydiae; however, the adequacy of viral-based controls may be questionable for diseases caused by protozoans and helminths (see Table D.6).

Consideration of all aspects of protozoan and helminth diseases--the etiologic agents, primary host, epidemiology, control measures, and incidence of infections in the United States, suggests that the enterovirus model can provide information useful for an assessment of protozoan and helminth research needs.

Rickettsial and chlamydial pathogens are not eliminated in feces, and therefore are not subject to transmission routes of enteric viruses. These forms are conveyed via arthropods and (in the case of Q fever) via food or respiratory tract transmissions. These forms are not pollutants in the sense of an enteric virus in which case one may find up to 10^6 logs of virus/g feces.

TABLE D.6 Diseases Caused by Protozoa and Helminths in the United States

Causative Organism	Disease	Host	Transmission Route
Balantidium coli	Balantidiasis	Man, Swine	Human, animal feces
Necator americanus	Hookworm	Man	Feces
Giardia lamblia	Giardiasis	Man	Feces
Enterobius vermicularis	Pinworm	Man	Feces
Trichuris trichiura	Whipworm	Man	Feces
Ascaris lumbricoides	Giant Roundworm	Man	Feces
Schistosoma mansoni	Schistosomiasis	Man, Snails	Feces, Water, Skin
Entamoeba histolytica	Amebiasis	Man	Feces
Hymenolepis nana	Dwarf tapeworm	Man	Feces
Taenia saginata[1]	Beef tapeworm	Man, Cattle	Feces
Taenia solium[1]	Pork tapeworm	Man, Swine	Feces

[1] Eggs found in feces of infected humans. Infection of primary animal hosts may result from exposure to food or water polluted by human feces. Principal source of infection of man is ingestion of undercooked or raw meat from an infected animal.

Enteropathogenic bacteria, found in the gastrointestinal tract of man and animals, can be compared with viruses, (especially Salmonella and Shigellia) in the sense that transmission routes may be identical. Important differences in epidemiological or infectious properties are related to (a) the qualitative number required for infection, (b) persistence in nature (i.e., shorter time), and (c) ease of transmission (i.e., usually not carried over long distances due to size, differences in adsorption capabilities, etc.).

GENERAL RECOMMENDATIONS

Top priority should be assigned to efforts to ensure the removal of enteric viruses from domestic wastewater. Attention should also be directed to efforts that will assure the freedom of finished waters from enteric viruses. Resources devoted to these objectives have not been adequate, and the need is immediate and great. Funds, laboratories, and viral experts should be mobilized and directed to carry out the research necessary to achieve these goals. Organization and conduct of research should be carried out on a scale which will make it possible to complete all necessary research within a five-year period.

In the interest of measures necessary for the protection of the public health, policies should be directed immediately toward the implementation of standards calling for less than 1 virus per 100 gallons of finished water, and less than 1 virus per 10 gallons of recreational water.

SPECIFIC RECOMMENDATIONS

Information on the presence of enteric viruses in water, sewage, crops, soil, and air has been compiled over the past four decades. Much of this information was obtained with methods which would be considered crude and incapable of a satisfactory degree of quantitation by present-day standards. Research to improve methods for the recovery, identification, and assay of enteric viruses from natural sources is needed to further advance knowledge regarding the presence and fate of viruses in the environment. Much of the (older) scientific literature dealing with the fate of viruses in the environment prior to 1965 should be reviewed and re-evaluated in the light of current technical capabilities and the newer concepts as a means of planning future research.

The endurance of viruses in environmental reservoirs for extended periods of time may be the result of replicative events rather than a passive survival capability. Knowledge of the ability of viruses to remain viable in the environment is important to determining needs for treatment of wastewaters.

Sufficient information on the occurrence and distribution of enteric viruses in the environment has been gathered to permit the following conclusion. Enteric viruses potentially are the most hazardous and the most difficult to detect of all the biological pollutants. Their ultramicroscopic size, the infectiousness of one infective unit, their invasiveness via aerosols, the potentially serious nature of the diseases they cause, their resistance to many environmental influences, and their transmission potential via solids, water, and air set them apart from other biological pollutants. The following recommendations are offered.

1. Research is needed to identify mechanisms contributing to aerosol production in wastewater treatment. Concurrently, the public health significance of virus survival and dissemination during spray irrigation should be determined. Virus adsorption, penetration, and survival on crops should be studied in order to understand the potential for infection resulting from a virus transmission process involving food crops.

2. Efforts should be made to further develop and improve methods for recovery of viruses from a variety of surface waters, fresh and saline. This should proceed simultaneously with the development of effective programs to ensure the high quality of public water supplies. Research to improve methods of virus detection should be directed initially to enteroviruses, reoviruses, and adenoviruses. Attention might be directed next to selected viruses which would serve as models for candidate oncogenic viruses, or "slow" viruses. These studies should emphasize the development of procedures for the rapid identification of these viruses to permit their recognition within 24 hours. The application of such measurements will greatly enhance the determination of the rate of transport of viruses in the environment.

3. Because of the role shellfish play as carriers of the viruses responsible for outbreaks of infectious hepatitis and possibly acute gastroenteritis, efforts must be continued to improve methodology for the detection of shellfish viruses. Those procedures most effective in the removal of viruses from commercial shellfish should be identified and measured for reliability. The role of estuarine sediments as reservoirs of enteric viruses from which induction of a virus residence phase in shellfish may proceed, should be studied.

4. Studies of virus destruction by disinfectants should be given high priority. Special attention should be directed to basic mechanisms; inactivation kinetics; the influence of solids-adsorbed viruses upon disinfection; and toxic, carcinogenic, and teratogenic side effects.

5. Consideration should be given to the training of the scientific personnel required for the conduct of research in environmental virology over the next two decades. Funds should be made available to appropriate university centers, and qualified state and public health laboratories should be encouraged to participate in monitoring and investigative efforts.

6. Enteric virus infectiousness in man needs to be reevaluated and the number of infectious units redefined in terms of virion aggregation and portal of entry. This information is needed for assessment of the relationship of health risk to numbers of viruses present.

7. Waste management practices should feature efforts to remove the virus hazard from the nation's surface waters. Top priority should be given to treatment of sewage wastes, since they represent the source point from which viruses pollute aquatic, terrestrial, and atmospheric environments. Projects should be initiated to test economically sound and scientifically valid methods for removing the virus hazard.

NOTE

1 J. Hornbeck, U.S. Forestry Service; R.Pierce, U.S. Forestry Service; T. Metcalf, University of New Hampshire, personal communication, 1976. Work completed under Grant Number FS-NE-1601, Maintaining Water Quality and Increasing Summer Stream Flow in New England Hard Wood Ecosystems.

REFERENCES

Berg, G. (1970) An integrated approach to the problem of viruses in water. Pages 339-346, Proceedings of National Specialty Conference on Disinfection. New York: American Society of Civil Engineers.

Berg, G. (1973) Reassessment of the virus problem in sewage and in surface and renovated waters. Progress in Water Technology 3:87-94.

Berg, G. (1976) Reclamation and disposal. Pages 253-255, Viruses in Water, edited by G. Berg, H.L. Bodily, E.H. Lennette, J.L. Melnick, and T.G. Metcalf. Proceedings of International Conference on Viruses in Water, Mexico City, 1974. Washington, D.C.: American Public Health Association.

Berg, G., R.B. Dean, and D.R. Dahling (1968) Removal of poliovirus 1 from secondary effluents by lime flocculation and rapid sand filtration. Journal of the American Water Works Association 60:193-198.

Biggs P., G. de-The, and L. Payne, eds. (1972) Oncogenesis and Herpes Viruses. International Agency for Research on Cancer. Lyons: World Health Organization.

Blacklow, N.R., R. Dolin, D.S. Fedson, H.L. Dupont, R.S. Northrup, R.B. Hornick, and R.M. Chanock (1972) Acute infectious non-bacterial gastroenteritis: Etiology and pathogenesis. Annals of Internal Medicine 76:993-1008.

Brungs, W.A. (1973) Effects of residual chlorine on aquatic life. Journal of the Water Pollution Control Federation 45:2180-2193.

Bryan, J.A., J.D. Lehmann, I.F. Setiady, and M.H. Hatch (1974) An outbreak of hepatitis-A, associated with recreational lake water. American Journal of Epidemiology 99:145-154.

Carlson, G.F., Jr., F.E. Woodard, D.F. Wentworth, and O.J. Sproul (1968) Virus inactivation on clay particles in natural waters. Journal of the Water Pollution Control Federation 40:89-106.

Cooper, R.C., J.L. Potter, and C. Leong (1974) Virus survival in solid waste treatment systems. Pages 218-240, Virus Survival in Water and Wastewater Systems, edited by J.F. Malina and B.P. Sagik. Center for Research in Water Resources. Austin: University of Texas.

Craighead, J.E. (1975) The role of viruses in the pathogenesis of pancreatic disease and diabetes mellitus. Progress in Medical Virology 19:162-214.

Craun, G.F. and L.J. McCabe (1973) Review of the causes of waterborne-disease outbreaks. Journal of the American Water Works Association 65:74-84.

Craun, G.F., L.J. McCabe, and J.M. Hughes (1975) Waterborne Disease Outbreaks in the United States, 1971-74. Denver: American Water Works Association.

Culp, G.L., R.L. Culp, and C.L. Hamann (1973) Water resource preservation by planned recycling of treated wastewater. Journal of the American Water Works Association 65:641-647.

DeFlora, S., G.P. DeRenzi, and G. Badolati (1975) Detection of animal viruses in coastal seawater and sediments. Applied Microbiology 30:472-475.

DeMichele, E. (1974) Water reuse, virus removal and public health. Pages 45-56, Virus Survival in Water and Wastewater Systems, edited by J.F. Malina and B.P. Sagik. Center for Research in Water Resources. Austin: University of Texas.

Dougherty, W.J. and R. Altman (1962) Viral hepatitis in New Jersey, 1960-61. American Journal of Medicine 32:704-736.

England, B., R.E. Leach, B. Aoame and R. Shiosaki (1967) Virologic assessment of sewage treatment at Santee, California. Pages 401-417, Transmission of Viruses by the Water Route, edited by G. Berg. New York: Interscience Publishers.

Gerba, C.P., M.D. Sobsey, C. Wallis, and J.L. Melnick (1974) Enhancement of poliovirus adsorption in wastewater onto activated carbon. Pages 115-126, Virus Survival in Water and Wastewater Systems, edited by J.F. Malina and B.P. Sagik. Center for Research in Water Resources. Austin: The University of Texas.

Gerba, C.P., C. Wallis, and J. L. Melnick (1975) Enteric viruses as biological pollutants. Environmental Science and Technology 9:1122-1126.

Grabow, W.O. (1968) The virology of wastewater treatment. Water Research 2:675-701.

Herrmann, J.E. and S.A. Morse (1973) Coupling of peroxidase to poliovirus antibody, characteristics of the conjugates and their use in virus detection. Infection and Immunity 8:645-649.

Homma A., M.D. Sobsey, C. Wallis, and J.L. Melnick (1973) Virus concentration from sewage. Water Research 7:945-950.

Kapikian, A.Z., J.L. Gerin, R.G. Wyatt, T.S. Thornhill, and R.M. Chanock (1973) Density in cesium chloride of the 27nm "8Flla" particle associated with acute infectious non-bacterial gastroenteritis: Determination by ultracentrifugation and immune electron microscopy. Proceedings of the Society for Experimental Biology and Medicine 42:874-877.

Katzenelson, E. (1976) Virologic and engineering problems in monitoring viruses in water. Pages 152-164, Viruses in Water, edited by G. Berg, H.L. Bodily, E.H. Lennette, J.L. Melnick, and T.G. Metcalf. Proceedings of the International Conference on Viruses in Water, Mexico City, 1974. Washington, D.C.: American Public Health Association.

Keller, J.W., R.A. Morin, and T.J. Schaffernoth (1974) Ozone disinfection pilot plant studies at Laconia, New Hampshire. Journal of the American Water Works Association 66(12):730-733.

Kirk, B.S., R. McNabney, and C.S. Wynn (1971) Pilot plant studies of tertiary wastewater treatment with ozone. 162nd National Meeting of American Chemical Society, September 12-17, Washington, D.C., Division of Environmental Chemistry, Preprint. Washington, D.C.: American Chemical Society.

Kruse, C.W., K. Kawata, V.P. Olivieri and K.E. Longley (1973) Improvements in terminal disinfection of sewage effluents. Water and Sewage Works 120:57-64.

Lund, E. (1971) Observations on the virus binding capacity of sludge. Pages 1-24, Advances in Water Pollution Research, edited by S.H. Jenkins. New York: Pergamon Press.

Lothrop, T.L. and O.J. Sproul (1969) High-level inactivation of viruses in wastewater by chlorination. Journal of the Water Pollution Control Federation 41:567-575.

Majumder, S.B. and O.J. Sproul (1974) Technical and economic aspects of water and wastewater ozonation: A critical review. Water Research 8:253-260.

Mason, J.O. and W.R. McLean (1962). Infectious hepatitis traced to the consumption of raw oysters: An epidemiological study. American Journal of Hygiene 75:1-22.

Mazur, B. and W. Paciorkiewicz (1974) The role of vegetables in dissemination of enteroviruses. I. The presence of poliovirus in overground parts of plants cultivated on soil containing the virus. Acta Microbiologica Polonica (A) 6:144. (Taken from Literature Abstracts, Viruses in Waste, Renovated and Other Waters, 1974). Office of Research and Development, Cincinnati, Ohio: U.S. Environmental Protection Agency.

Metcalf, T.G. (1975) Role of viruses in management of environmental risks. Presented at Conference on Management of Wastewater Residuals, Williamsburg, Virginia, November 13-14, 1975. National Science Foundation-RANN. Washington, D.C.: National Science Foundation.

Metcalf, T.G. (1976) Viral Monitoring of Commercial Shellfish. Technical Progress Report. Food and Drug Administration, U.S. Public Health Service, Washington, D.C.: Department of Health, Education and Welfare.

Metcalf, T.G. and W.C. Stiles (1965) The accumulation of enteric viruses by the oyster, Crassostrea virginica. Journal of Infectious Diseases 115:68-76.

Mosley, J. (1965) Transmission of viral diseases by drinking water. Pages 5-23, Transmission of Viruses by the Water Route, edited by G. Berg. New York: Interscience Publishers.

Olivieri, V.P., T.K. Donovan, and K. Kawata (1970) Inactivation of virus in sewage. Pages 365-383, Proceedings of the National Specialty Conference on Disinfection. New York: American Society of Civil Engineers.

Palfi, A. (1972) Survival of enteroviruses during anaerobic sludge digestion. Pages 99-104, Proceedings of the Sixth International Water Pollution Research Conference. Oxford: Pergamon Press.

Pavoni, J.L. and M.E. Tittlebaum (1974) Virus inactivation in secondary wastewater treatment plant effluent using ozone. Pages 180-197, Virus Survival in Water and Wastewater Systems, edited by J.F. Malina, Jr. and B.P. Sagik. Center for Research in Water Resources. Austin: University of Texas.

Peterson, M.L. (1974) Soiled disposable diapers: A potential source of viruses. American Journal of Public Health 64:912-914.

Plotkin, S.A. and M. Katz (1965) Minimal infective doses of viruses for man by the oral route. Pages 151-166, Transmission of Viruses by the Water Route, edited by G. Berg. New York: Interscience Publishers.

Roos, B. (1956) Hepatitis epidemic conveyed by oysters in Sweden. Lakartidningen 53:989-1003.

Ruddy, S.J., R.F. Johnson, J.W. Mosley, J.B. Atwater, M.A. Rossetti, and J.C. Hart (1969) An epidemic of clam-associated hepatitis. Journal of the American Medical Association 208:649-655.

Sattar, S.A., S. Ramia, and J.C.N. Westwood (1974) Removal and inactivation of poliovirus during lime (calcium hydroxide) treatment of sewage. I.R.C.S. [International Research Communication Systems[Journal of Medical Sciences (Biomedical Technology; Microbiology) 2:1635.

Schaub, S.A. and B.P. Sagik (1975) Association of enteroviruses with natural and artificially introduced colloidal solids in water and infectivity of solids-associated virions. Applied Microbiology 30:212-222.

Shuval, H.I., S. Cymbalista, A. Wachs, Y. Yohar, and N. Goldblum (1966) The inactivation of enteroviruses in sewage by chlorination. Advances in Water Pollution Research 2:1-8.

Slanetz, L.W., C.H. Bartley, T.G. Metcalf, and R. Nesman (1971) Survival of enteric bacteria and viruses in municipal sewage lagoons. Pages 132-140, Proceedings of the 2nd International Symposium for Waste Treatment Lagoons. Kansas City, Mo.: Missouri Basin Engineering Health Council and the Federal Water Quality Administration.

Sobsey, M.D. and R.C. Cooper (1973) Enteric virus survival in algal-bacterial wastewater treatment systems: I. Laboratory studies. Water Research 7:669-685.

Sobsey, M.D., C. Wallis, and J.L. Melnick (1975) Development of a simple method for concentrating enteroviruses from oysters. Applied Microbiology 29:21-26.

Sorber, C.A. (1973) Protection of the public health. Pages 201-209, Proceedings of the Conference on Land Disposal of Municipal Effluents and Sludges. EPA-902/9-73-001. New York: U.S. Environmental Protection Agency, Region II; PB 227 115. Springfield, Va.: National Technical Information Service.

Sorber, C.A., S.A. Schaub and K.J. Guter (1972) Problem Definition Study: Evaluation of health and hygiene aspects of land disposal of wastewater at military installations. Frederick, Md.: U.S. Army Medical Bioengineering Research and Development Command.

Taylor, F.B. (1974) Viruses--What is their significance in water supplies? Journal of the American Water Works Association 66:306-311.

U.S. Department of Health, Education and Welfare (1975) Hepatitis Surveillance 1975. Report No. 37. Atlanta: Center for Disease Control.

Westwood, J.C.N. and S.A. Sattar (1976) The minimal infective dose. Pages 61-69, Viruses in Water, edited by G. Berg, H.L. Bodily, E.H. Lennette, J.L. Melnick, and T.G. Metcalf. Proceedings of the International Conference on Viruses in Water, Mexico City, 1974. Washington, D.C.: American Public Health Association.

Wright, K.A. and J.G. Trump (1956) High energy electrons for the irradiation of blood derivatives. Pages 230-239, Proceedings of the 6th Congress of the International Society of Blood Transfusion. Paris: International Society of Blood Transfusion.

Zillick, J.A. (1972) Toxicity of combined chlorine residuals to freshwater fish. Journal of the Water Pollution Control Federation 44:212-220.

BIBLIOGRAPHY

Duboise, S.M., B.P. Sagik, and J.F. Malina, Jr. (1974) Virus migration through soils. Pages 233-240, Virus Survival in Water and Wastewater Systems, edited by J.F. Malina and B.P. Sagik. Center for Research in Water Resources. Austin: University of Texas.

Dugan, G.L., R.H. Young, L.S. Lau, P.C. Ekern, and P.C. Loh (1975) Land disposal of wastewater in Hawaii. Journal of the Water Pollution Control Federation 47:2067-2087.

Newton, W.L. (1950) Water treatment measures in control of amebiasis. American Journal of Tropical Medicine 30:135-138.

Newton, W.L. and M.F. Jones (1949) The effect of ozone in water on cysts of *Endamoeba histolytica*. American Journal of Tropical Medicine 29:681-699.

Newton, W.L., W.B. Figgat, and S.R. Weibel (1948) The effects of sewage treatment processes upon ova and miracidia of *Schistosoma japonicum*. Sewage Works Journal 20:657-664.

Newton, W.L., H.J. Bennett, and W.B. Figgat (1949) Observations on the effects of various sewage treatment processes upon eggs of *Taenia saginata*. American Journal of Hygiene 49:166-175.

Romero, J.C. (1970) The movement of bacteria and viruses through porous media. Ground Water 8:37-48.

Schaub, S.A., E.P. Meier, J.R. Kolmer, and C.A. Sorber (1975) Land application of wastewater: The fate of viruses, bacteria, and heavy metals at a rapid infiltration site. Frederick, Md.: U.S. Army Medical Bioengineering Research and Development Laboratory.

Sorber, C.A., S.A. Schaub, and H.T. Bausum (1974) An assessment of a potential virus hazard associated with spray irrigation of domestic wastewaters. Pages 241-252, Virus Survival in Water and Wastewater Systems, edited by J.F. Malina, Jr. and B.P. Sagik. Center for Research in Water Resources. Austin: University of Texas.

Wellings, F.M., A.L. Lewis, and C.W. Mountain (1974) Virus survival following wastewater spray irrigation of sandy soils. Pages 253-260, Virus Survival in Water and Wastewater Systems, edited by J.F. Malina, Jr. and B.P. Sagik, Center for Research in Water Resources. Austin: University of Texas.

Wellings, F.M., A.L. Lewis, and C.W. Mountain (1975) Pathogenic viruses may thwart land disposal. Water and Wastes Engineering 12:70-74.

Young, R.H.F. and N.C. Burbank, Jr. (1973) Virus removal in Hawaiian soils. Journal of the American Water Works Association 65:598-604.